THE UNIVERSITY OF ALBERTA

I. EVIDENCE FOR A PEREPOXIDE INTERMEDIATE IN THE REACTION OF β-HALOHYDROPEROXIDES WITH BASE.
II. STUDIES ON TRICYCLIC DIOXETANES.

BY

© PETER ALAN LOCKWOOD

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING 1977

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled

"I. EVIDENCE FOR A PEREPOXIDE INTERMEDIATE IN THE REACTION OF β-HALOHYDROPEROXIDES WITH BASE.
II. STUDIES ON TRICYCLIC DIOXETANES"

submitted by PETER ALAN LOCKWOOD in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Karl B. Roberts
Supervisor

Gary Karlich

A. S. Brown

William Hodgson

R. W. Jennings
External Examiner

DATE April 14, 1977

TO MY PARENTS

A B S T R A C T

In order to study migration of the hydroperoxy group on treatment of β-halohydroperoxides with base, the halohydroperoxides of isopropylidenecyclopentane, 16, were prepared. 1-(1-Bromo-1-methylethyl)cyclopentyl hydroperoxide, 11, the iodo compound, 15, and a mixture of 1-(1-chloro-1-methylethyl)cyclopentyl hydroperoxide, 14, and 1-(1-hydroperoxy-1-methylethyl)cyclopentyl chloride, 28, were converted to their crystalline p-nitrobenzoate esters. Treatment of either the β-halohydroperoxides or their peresters with base gave two allylic hydroperoxides, 1-(methylvinyl)cyclohexyl hydroperoxide, 13, and 1-(1-hydroperoxy-methylethyl)cyclopentene, 12, with the allylic hydroperoxide containing the migrated hydroperoxy group, 12, being formed in at least 70% yield. The product ratio 12/13 was hardly affected by the halogen leaving group. This hydroperoxy migration can be explained exclusively by a perepoxide intermediate.

The same allylic hydroperoxides, 12 and 13, were produced by reaction of 16 with singlet oxygen and triphenylphosphite ozonide but a perepoxide intermediate is not involved in these reactions. A possible mechanism for the reaction of triphenylphosphite oxonide with olefins is discussed.

1(5)-Bicyclo[3.3.0]octene, 58, 1(7)-bicyclo[5.3.0]-decene, 66, and 1(8)-bicyclo[6.4.0]dodecene, 74, were

prepared and 58 and 66 were converted to tricyclic dioxetanes, 9,10-dioxa[3.3.2]propellane, 48, and 11,12-dioxa-[5.3.2]propellane, 49, respectively, by treatment of the iodohydroperoxides of 58 and 66 with silver acetate. No halohydroperoxide or dioxetane of 74 could be prepared. The activation energies for the thermolysis of 48 and 49 were 24.5 and 29.8 kcal mole^{-1}, respectively, and the singlet and triplet excited state yields of 48 and 49 were 0.0066 and 0.084, and 0.0012 and 0.125, respectively.

The three known tricyclic dioxetanes, 48, 49 and 11,12-dioxa[4.4.2]propellane, 42, all show different energy partitioning between triplet and singlet state products produced on thermolysis, $^3\Phi/^1\Phi$ being 3115, 13 and 104 for 42, 48 and 49, respectively. It was not possible to determine if this effect was due to strain in the thermolysis products but this behaviour of tricyclic dioxetanes must be explained by any mechanism purporting to explain dioxetane thermolysis and chemiluminescence.

ACKNOWLEDGEMENTS

The author wishes to thank his research supervisor Dr. K. R. Kopecky for his advice and encouragement throughout this work. Dr. Kopecky was always available for discussion and my association with him has left a permanent impression.

The author is indebted to the National Research Council of Canada and to the University of Alberta and the Department of Chemistry for financial assistance.

The author would like to thank Mr. R. N. Swindlehurst, Dr. T. T. Nakashima and Dr. A. M. Hogg and their staffs for providing superior spectral and spectrometric data, and also Mrs. Darlene Mahlow for the microanalyses.

The author would also like to thank all the graduate and undergraduate students and postdoctoral fellows who have provided a congenial working atmosphere. Special thanks go to Professor F. P. Robinson, University of Victoria.

Special thanks to Mrs. Mary Waters for typing this thesis and for her experienced editorial advice.

Finally, words cannot express my gratitude to my wife Marian for her constant support and encouragement.

TABLE OF CONTENTS

Page

CHAPTER I

EVIDENCE FOR A PEREPOXIDE INTERMEDIATE IN THE REACTION OF β-HALOHYDROPEROXIDES WITH BASE

INTRODUCTION..... 1

RESULTS..... 14

DISCUSSION..... 24

EXPERIMENTAL..... 31

CHAPTER II

STUDIES ON TRICYCLIC DIOXETANES

INTRODUCTION..... 46

RESULTS..... 60

DISCUSSION..... 98

EXPERIMENTAL..... 111

BIBLIOGRAPHY..... 137

LIST OF TABLES

Table		Page
I	Product Distribution from the Allylic Hydroperoxide-forming Reactions Studied	21
II	Composition of the Allylic Hydroperoxide Mixtures	25
III	Decomposition of 9,10-Dioxa[3.3.2]propellane, 48, in Benzene at 45.1°C	75
IV	Decomposition of 11,12-Dioxa[5.3.2]propellane, 49, in Toluene at 93.7°C	76
V	Rate Constants for the Decomposition of 48 and 49	80
VI	Activation Parameters for the Thermolysis of 1,2-Dioxetanes	82
VII	Results of Temperature-Change Experiments on 48 in Benzene at 44.8°C and 24.8°C with DPA	84
VIII	Variation of Chemiluminescence Intensity of 48 with the Concentration of Added DPA in Benzene at 25°C	88
IX	Variation of Chemiluminescence Intensity of 48 with the Concentration of Added DBA in Benzene at 25°C	89
X	Slopes and Intercepts of the Double Reciprocal Plots of Chemiluminescence Intensity and Fluorescer Concentration in Benzene	92

Table		Page
XI	Yields of Excited State Carbonyl Products from Thermolysis of 1,2-Dioxetanes in Benzene Solution	97
XII	Energy Available from Themolysis of 1,2-Dioxetanes	102
XIII	Excited State Yields from Several Dioxetanes	108

LIST OF FIGURES

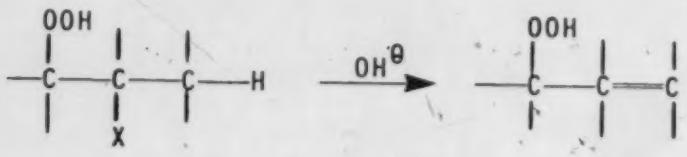
Figure		Page
1	Energy Available ($\mathcal{E}$) from Decomposition of 1,2-Dioxetanes	57
2	Rate of Decomposition of 48 in Benzene at 45.1°C	77
3	Rate of Decomposition of 49 in Toluene at 93.7°C	78
4	Effect of Fluorescer Concentration on the Relative Intensity of Chemiluminescence from 48.	90
5	Schematic Diagram of the Energetics of Dioxetane Decomposition based on the Biradical Mechanism of Richardson (59,89)	104

CHAPTER I

Evidence for a Perepoxide Intermediate in the Reaction of β-Halohydroperoxides with Base

I N T R O D U C T I O N

This project was carried out in order to clarify the mechanism of the reaction between β-halohydroperoxides and base, eq. [1] and to confirm the intermediacy of a

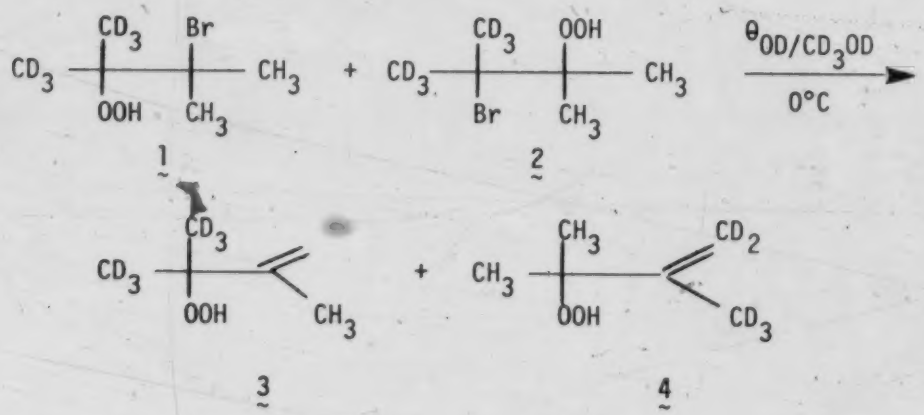
[1] 

peroxide in this reaction.

Most of the literature prior to 1973 in this and the related areas that will be discussed, has been reviewed by van de Sande (1), Scott (2) and Kopecky and van de Sande (3).

The formation of allylic hydroperoxides on treatment of β-halohydroperoxides with base is not a general reaction, succeeding only with β-halohydroperoxides of tetrasubstituted olefins. Treatment of less substituted β-halohydroperoxides with base results in formation of other products, some of which are formed from dioxetanes (4). In fact, treatment of di- and tri- substituted β-halohydroperoxides with base has been used to prepare dioxetanes (5).

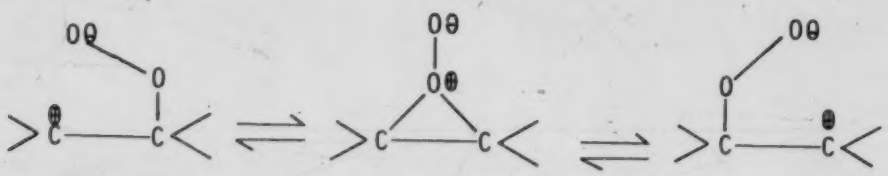
What is the mechanism of the reaction of tetrasubstituted β-halohydroperoxides with base? van de Sande (1,3) found that the hydroperoxy group of β-bromohydroperoxides migrates in the presence of base. His results are shown in eq. [2].

[2] 

1/2 = 0.63 3/4 = 2.2

Kopecky and van de Sande (1,3) proposed several possible mechanisms for the formation of rearranged product in eq. [2]. One of these mechanisms involved a dioxetane intermediate but this was dismissed (3) when it was observed that tetramethyldioxetane was stable under the elimination reaction conditions (5). A second mechanism involved a fragmentation of the halohydroperoxide to an olefin and singlet oxygen which then recombined to form the allylic hydroperoxides. Evidence against this mechanism was also presented (3). Kopecky and van de Sande also considered the possibility that a pair of rapidly intercon-

verting zwitterions as shown below could account for the



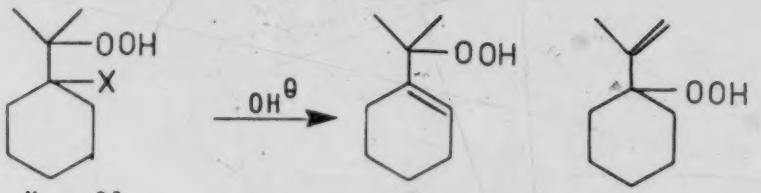
hydroperoxy group migration. This mechanism was ruled out since there should be such a difference in the stabilities of the zwitterions obtained on treatment of 3-bromo-3-methyl-2-(4-methoxyphenyl)2-butyl hydroperoxide with base that only the allylic hydroperoxides from the zwitterion with the benzylic carbonium ion would be expected as the product. However, both possible allylic hydroperoxides are obtained and so Kopecky and van de Sande (3) concluded that migration of the hydroperoxy group on treatment of β-halohydroperoxides with base was best explained by formation of a perepoxice intermediate and conversion of this perepoxide to the allylic hydroperoxides without the involvement of a zwitterion.

Kopecky and van de Sande (1,3) also showed that no direct elimination was occurring when a mixture of 1 and 2 was treated with base since the ratio of 1 to 2 remained constant over the course of the reaction. This would not occur if direct elimination was involved since the isotope effect would cause 1 to react faster than 2.

In order to obtain more information about the existance of a perepoxide intermediate in these reactions, Scott (2) studied the reactions of the halohydroperoxides

5,6, and 7 with base, eq. [3].

[3]

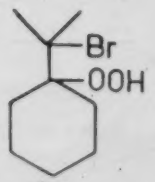


5, X = Cl

6, X = Br

7, X = I

Scott found that the ratio of 8/9 was about 15 no matter which halogen was used. Not surprisingly the reaction of base with the p-nitrobenzoate ester of 5 gave the same result. The ratio 8/9 = 15 means that the product mixture was 94% 8 and only 6% 9. However, the fact that 9 was present at all implied that migration of the hydroperoxy group had taken place. This was attributed (2) to a perepoxide intermediate.



10

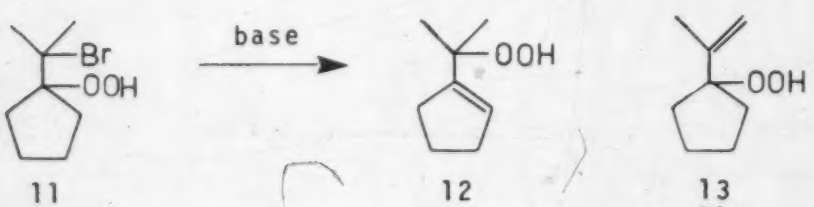
Baldwin and Lever (6) also studied the reaction of 6 with base. They reportedly prepared two different mixtures of 6 and its isomer 10 and treated these mixtures with base. From n.m.r. measurements they found that the ratio of 8/9 was the same as the ratio of starting materials

6/10 and concluded that no migration of the hydroperoxy group had taken place.

However, Baldwin never purified his bromohydroperoxides or separated them; neither did he isolate or purify the resultant allylic hydroperoxides. Scott used pure, single isomers in his experiments. Scott (2) also found no trace of 10 in his preparation of 6 while Baldwin reported that, under conditions similar to those of Scott, he obtained about 20% 10. Baldwin's (6) conclusions do not agree with those of Scott (2) or with those presented in this chapter which confirm and expand the results of Scott.

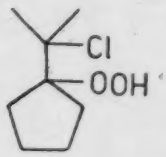
Preliminary results of Scott (2) showed that in the reaction of the β-bromohydroperoxide of isopropylidenecyclopentane, 11, with base, eq. [4], the ratio of 12 to 13 was much closer to one and would therefore provide better evidence for migration and a perepoxide intermediate than could be obtained in the analogous isopropylidenecyclohexane series.

[4]

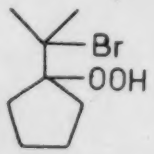


11 12 13

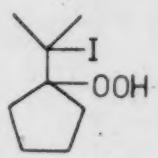
This chapter, then, deals with a study of the β-halohydroperoxides of isopropylidenecyclopentane 14, 11, 15, and their reactions with base.



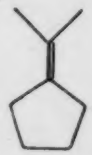
14



11



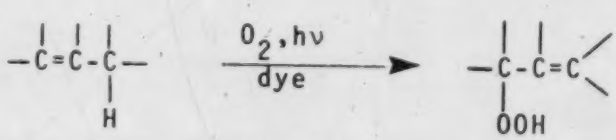
15



16

For comparison purposes, the 12/13 ratios for the reaction of 16 with singlet oxygen (via photosensitized oxygenation) and with triphenylphosphite ozonide were also measured.

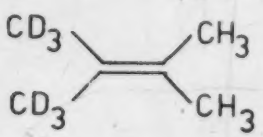
The question of the existance of a perepoxide has been investigated mainly in connection with the mechanism of photosensitized oxygenation of olefins. Sharp (7) and Kopecky and Reich (8) proposed that the perepoxide was an intermediate in the reaction between singlet oxygen and an olefin to yield allylic hydroperoxides, eq. [5].

[5] 

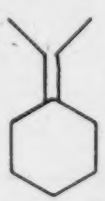
Kearns (9) provided evidence for the existance of a perepoxide in this reaction by supposedly trapping it with azide ion to form an azidohydroperoxide. However Foote (10) showed that the amount of azidohydroperoxide

produced depends on the sensitizer used and also that the azido compound could be formed in a free radical reaction. Foote concluded that there was no common intermediate in the production of the allylic hydroperoxides and the azidohydroperoxides. Gollnick (11) has also presented evidence that the azidohydroperoxides were formed in a free radical reaction. Kearns (12) later found basically the same result.

Kopecky and van de Sande (3) had proposed that the allylic hydroperoxides produced in the reaction of β-halohydroperoxides with base were formed via a perepoxide intermediate. However they found that in the photosensitized oxygenation of 17, the ratio of allylic hydroperoxides 3



17

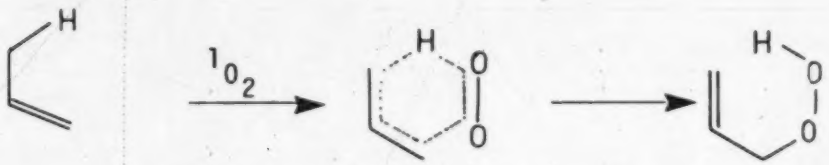


18

and 4 was significantly different from the same ratio from the halohydroperoxide reaction, eq. [2]. This led to the conclusion that a common intermediate was not involved in the two reactions and since a perepoxide was implicated in the halohydroperoxide reaction it could not be the intermediate in the photooxidation. This result was confirmed by Scott's (2) study on isopropylidenecyclohexene, 18,

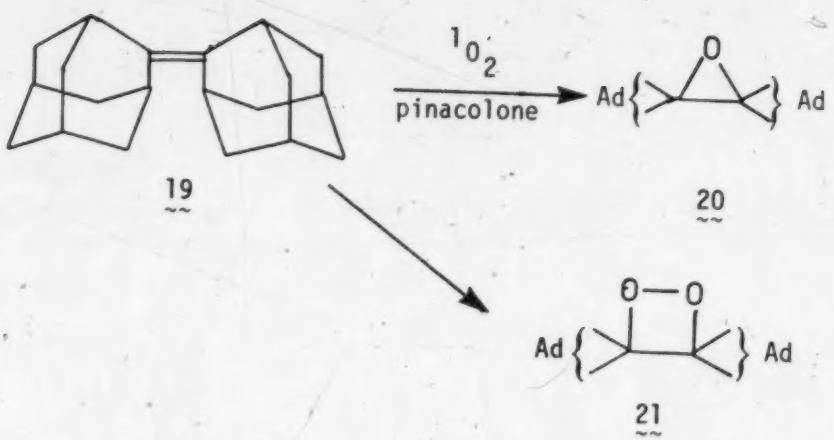
where he showed that different product ratios were obtained from the photooxidation and β-halohydroperoxide elimination reactions. The 8/9 ratios are 15 for the elimination reaction and 0.11 for the photooxygenation.

With the existance of the perepoxide intermediate apparently disproven, the mechanism commonly accepted by most authors, for example (13-16), is the concerted mechanism involving a 6-centered transition state due to Nickon (17,18), eq. [6].

[6] 

However, the proposal that a perepoxide intermediate was involved in photooxidation reactions did not die. In 1973, Schaap and Faler (19) obtained some adamantylidene-adamantane epoxide, 20, in the photosensitized oxygenation of adamantylideneadamantane, 19, the major product of the reaction being the dioxetane, 21, eq. [7].

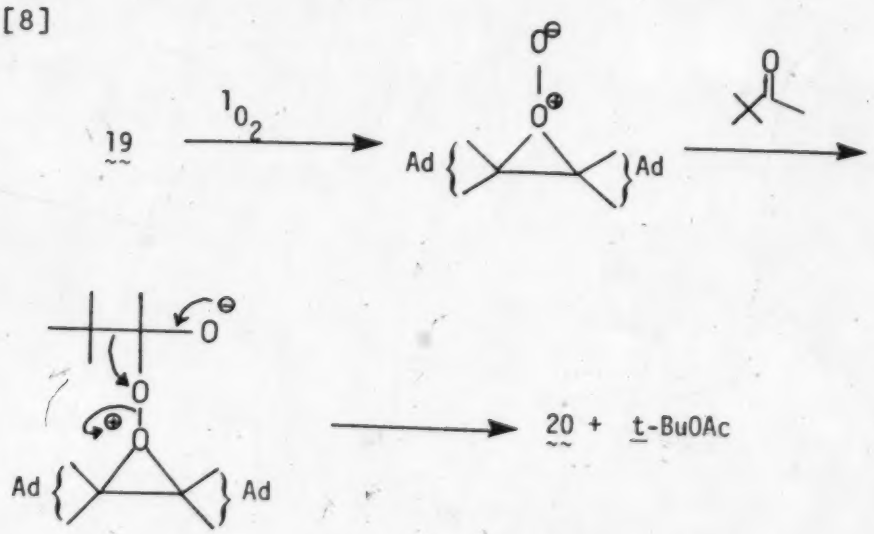
[7]



19 20 21

Schaap (19) also found that t-butyl acetate was formed in this reaction and he attributed the formation of this and 20 to the reduction of a perepoxide in a Baeyer-Villiger-type reaction, eq. [8].

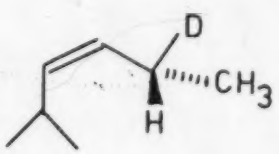
[8]



However, Jefford and Boschung (20) repeated Schaap's experiment and found that the yield of epoxide was dependent on the sensitizer and furthermore no t-butyl acetate could be detected. Jefford (10) also showed that radicals were involved in the formation of 20 since with rose bengal as sensitizer the photoxidation gave mainly 20 as the product, but when the radical trap di-t-butyl-p-cresol was added, only the dioxetane, 21, was formed.

As additional evidence, Jefford and Boschung (21) showed that photooxidation of norbornene using methylene blue gave very low yields of dioxetane and epoxide. However, photooxygenation in pinacolone did not increase the yield of epoxide or result in the production of any t-butyl acetate.

Similarly, Bartlett and Ho (22) photooxygenated 7,7'-binorbornylidene in a variety of solvents and using several sensitizers they obtained varying amounts of epoxide and dioxetane. However, since more epoxide was produced in benzene than in pinacolone they concluded that a Baeyer-Villiger process as outlined in eq. [8] did not occur.



22

In the photooxygenation of 22, Stephenson (23) compared the deuterium/hydrogen ratio to the R/S ratio in the product allylic hydroperoxides. Using acetone as the solvent the two ratios were equal but in methanol they were not. They attributed this difference to a perepoxide intermediate being intercepted by a molecule of solvent methanol in an assisted β-elimination and showed that this mechanism could explain the difference in the D/H and R/S ratios. On the other hand, the concerted mechanism for allylic hydroperoxide formation was shown to always result in equal D/H and R/S ratios. Note that Stephenson's work does not provide direct evidence for a perepoxide, but it was proposed since it provides the simplest explanation of the results.

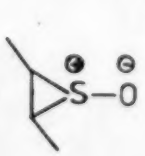
Dewar and co-workers (24,25) and Inagaki and Fukui (26) have shown using theoretical calculations that a perepoxide-like intermediate would not be unexpected in photosensitized oxygenation. Dewar (24) in fact, goes so far as to say that, in the case of photooxidation of olefins not carrying electron-withdrawing substituents, both allylic hydroperoxides and dioxetanes are formed from the perepoxide. As experimental evidence for his theoretical arguments, Dewar relies heavily on the work of Schaap (19) on 19 discussed earlier and later shown to be incorrect (20). It should also be noted that

Dewar's calculations deal only with simple olefins, ethylene and propylene, which are difficult to photooxygenate. In fact, the structure of the olefin may influence the calculations and the experiments considerably.

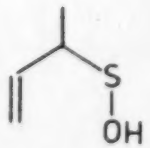
Dewar's (24) attempt to discount the conclusion of Kopecky and van de Sande (3) that only a perepoxide was involved in the reaction between the bromohydroperoxide of tetramethylethylene and base appears ill-founded since the mechanism proposed by Dewar involves a direct elimination already ruled out by Kopecky and van de Sande as discussed earlier.

Several other reports of perepoxide intermediates have been made in the literature (27-29) but these are based mainly on speculation.

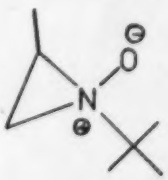
Baldwin (30,31) and Kondo (32) have reported compounds that have structures which are analogous to that of the perepoxide and so provide precedent for consideration of the perepoxide as an intermediate. Episulphoxides (30,32) and aziridine-N-oxides, when suitably substituted, react on heating to give products which are analogous to allylic hydroperoxides. For example 23 gives 24 and



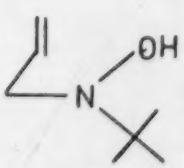
23



24



25



26

25 gives 26.

Triphenyl phosphite ozonide (33) is known to decompose to triphenyl phosphite and singlet oxygen at -20°C (34,35). However, at -70°C olefins react with triphenyl phosphite ozonide to form allylic hydroperoxides without the intervention of singlet oxygen as a reagent (35).

Using the same arguments for concluding that photooxidation did not involve a perepoxide, Kopecky and van de Sande (3) showed that reaction of 17 with triphenyl phosphite ozonide at -70°C did not involve a perepoxide since this reaction gave different results than the reaction of 1 and 2 with base. Similarly, Scott (2) found that when 18 was treated with triphenyl phosphite ozonide at -70°C the produced ratio 8/9 was different than that obtained when 6 was treated with base (from triphenyl phosphite ozonide 8/9 = 0, from halohydroperoxide elimination 8/9 = 15), and he concluded that no perepoxide was involved in the triphenyl phosphite ozonide reaction.

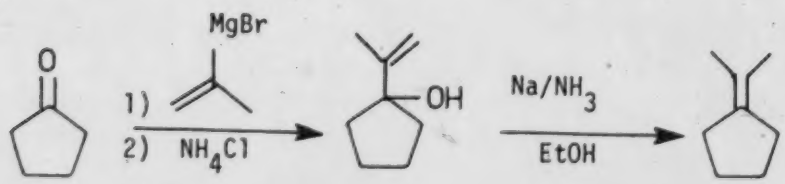
It appears that neither a perepoxide nor a singlet oxygen reaction can explain the reaction between triphenyl phosphite ozonide and olefins below -40°C.

RESULTS

Preparation of Isopropylidenecyclopentane, 16:

The olefin was synthesized in 29% yield following the method of Scott (2) as outlined in eq. [9].

[9]



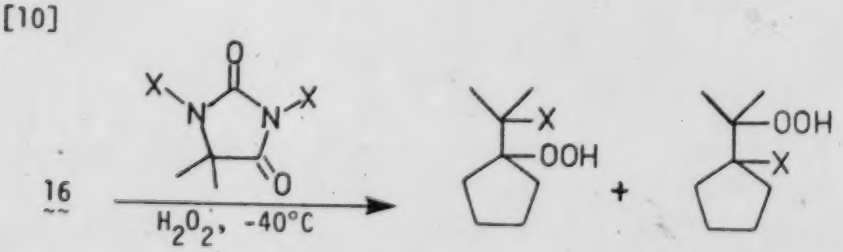
27 16

The structures of 27 and 16 were confirmed by comparison with published data (2,37).

Preparation of the β-Halohydroperoxides of 16.

The β-halohydroperoxides of isopropylidenecyclopentane, 16, were all prepared in basically the same way using the method of van de Sande (1), eq. [10].

[10]



14, X = Cl 28, X = Cl
11, X = Br 19, X = Br
15, X = I 30, X = I

Although eq. [10] shows that two possible products could be formed in each case, only when X = Cl were both products actually obtained.

The bromohydroperoxide, 11, was purified by low temperature crystallization from isopentane to yield a white solid, mp. -5°C to -10°C, with a purity of 99.2% as determined by iodometric titration.

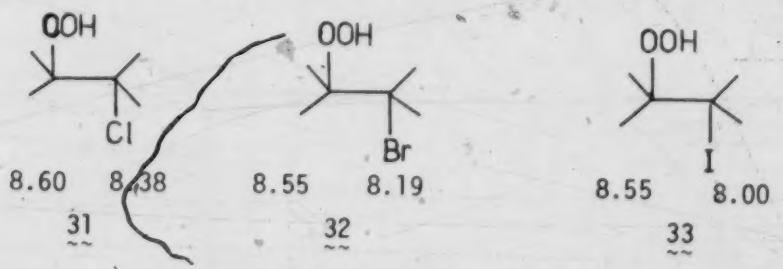
The chlorohydroperoxide mixture 14 + 28 could not be purified by either low temperature crystallization or repeated low temperature column chromatography. Samples from chromatography were at best only 93% pure by iodometric titration. This problem with chlorohydroperoxides of olefins appears general, many products being formed in this as well as other (39) cases and the complex mixtures of similar compounds (dichlorides, etc.) are difficult to separate. In the chlorohydroperoxide mixture 14 predominates but more accurate estimation of the 14/28 ratio proved impossible since the mixture was not pure.

DANGER

15 exploded violently when isolated pure and solvent-free! DO NOT remove the solvent from pure material! 14 and 11 appear to be more stable than 15 but should be considered potential explosives.

The iodohydroperoxide 15 was purified by low temperature chromatography to yield a material that was 98% pure by iodometric titration. Removal of all solvent at -20°C under vacuum resulted in an oil which exploded when warmed up. Only a few milligrams in a disposable pipette detonated with a very loud report and total disintegration of the pipette.

Structural assignments of the β-halohydroperoxides were made on the basis of their n.m.r. spectra. The positions of the gem-dimethyl signal in the spectra of 14, 28, 11 and 15 allowed their structure to be determined by analogy with compounds prepared by van de Sande (1) and Filby (5,37) shown below.



31 32 33

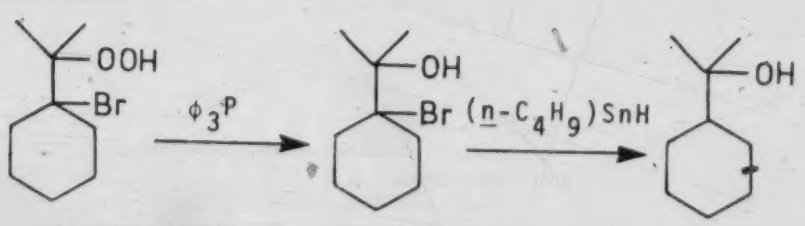
The values shown are the chemical shifts in τ of the signals of the gem-dimethyl groups directly above.

The bromohydroperoxide of 16 showed a gem-dimethyl absorption at τ 8.12 in the n.m.r. spectrum and so by analogy with 32 was assigned structure 11. Similarly, the iodohydroperoxide was assigned structure 15 due to its gem-dimethyl signal at τ 7.94. The chlorohydroperoxide showed gem-dimethyl absorptions at τ 8.33 and τ 8.54 and

and was thus assumed to be a mixture of 14 and 28.

The validity of this method of structure assignment based on the positions of the gem-dimethyl absorptions in the n.m.r. spectra was proven by Scott (2) using 6. He assigned the structure of 6 using the n.m.r. method just outlined and then confirmed the structural assignment independently as shown below, eq. [11].

[11]



6 34 35

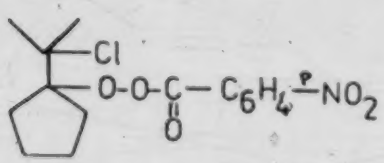
Scott obtained 35 as a product as shown in eq. [11] and 35 could only have been formed if the starting material was 6 not 10. This chemical sequence confirms the structure of the bromohydroperoxide as 6, in agreement with the structure assigned on the basis of the n.m.r. spectrum.

Preparation of the p-Nitrobenzoate Esters of 11, 14, 28 and 15:

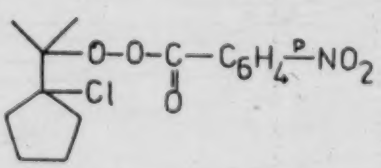
Although the bromohydroperoxide, 11, proved easy enough to purify and handle, the chlorohydroperoxide mixture 14 + 28 could not be purified and the iodohydroperoxide, 15, was too dangerous to use in its pure state.

It was known that 1,4-diazabicyclo[2.2.2]octane (DABCO) forms a complex with hydroperoxides (40) and this method had been used in the purification of halohydroperoxides of ethylidinecyclohexane (41). However, no complex of 14 + 28 or 15 with DABCO could be isolated. However, it now appears that a DABCO complex of 14 + 28 has been isolated by Kopecky (39), but it has not been characterized.

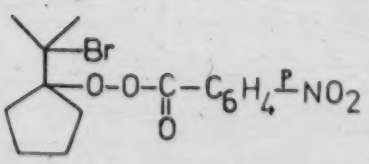
Scott had prepared a p-nitrobenzoate of 5 and found that the results from reaction of base with the perester were the same as the results obtained with the underivatized chlorohydroperoxide, so the p-nitrobenzoate esters of 11, 14 + 28 and 15 were prepared by the route normally used for alcohols (42) and the peresters were all purified by low temperature chromatography and by recrystallization. The peresters corresponding to 11, 14 + 28 and 15 are 38, 36 + 37 and 39, respectively.



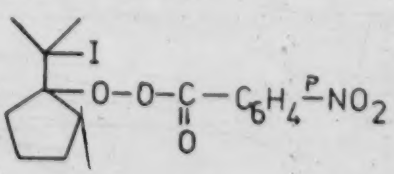
36



37



38



39

The structures of the peresters were all confirmed by the similarity of their n.m.r. spectra with those of their parent compounds and by microanalysis.

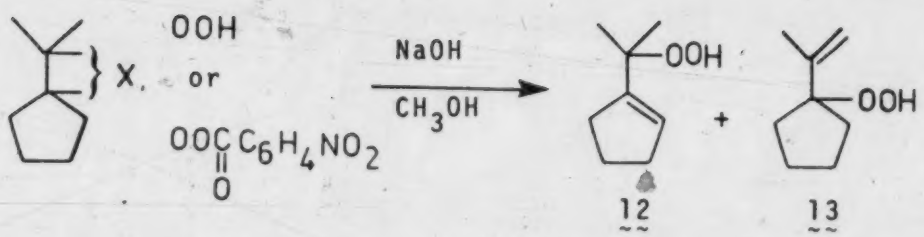
The peresters could not be analyzed in the normal fashion by iodometric titration since they reacted only very slowly with potassium iodide solution. This fact is in line with the work of Mair (43) who also found peresters to be only slightly reactive towards iodide.

The n.m.r. spectrum of the chloroperester mixture 36 + 37 was clear enough that the 36/37 ratio could be estimated as 3/1 using the integrations of the gem-dimethyl signals.

Reactions of the β-Halohydroperoxides and β-Haloperoxy-p-nitrobenzoates with Base:

Initially the 12/13 ratios were obtained by treating the substrate 11, 38, 36 + 37 or 39 with one equivalent of base in methanol and then extracting the allylic hydroperoxides following the procedure of Scott (2). However, since this method did not permit isolation of quantitative yields of 12 and 13, the n.m.r. spectral method described in the experimental section was used. The reaction is outlined in eq. [12].

[12]



12 13

12 and 13 must be the only products formed in eq. [12] since, as can be seen in Table I, the yield of 12 + 13 as measured by n.m.r. using an internal standard can account for all the halohydroperoxide used as starting material. This conclusion is also in agreement with Scott (2), Filby (38) and van de Sande (1) all of whom have shown that treatment of β-halohydroperoxides with base gives quantative yields of allylic hydroperoxides.

The 12/13 ratios were determined by amplification of the olefinic region of the n.m.r. spectrum and comparison of the integrals for the olefinic signals of 12 and 13. 12 showed a triplet at τ 4.40 and 13 a complex multiplet at τ 5.10. These assignments were made by analogy with 8 and 9 which had olefinic absorptions at τ 4.35 and τ 5.05, respectively (2). Also cyclopentene has its olefinic absorption at τ 4.40 (44). The results are presented in Table I.

TABLE I

Product Distribution from the Allylic Hydroperoxide-forming Reactions Studied[a]

Substrate	Concentration [M]	Reagent	Solvent	Temperature (°C)	Relative areas[b] 12[c]	13[c]	Reference[d]	Yield (%) of 12 + 13[e]	12/13	12:13[k]
11	0.20	NaOD(0.43 M)	CD_3OD	22°	1.41	1.15	4.20	101	2.45	71 : 29
38	0.20	NaOD(0.30 M)	CD_3OD	22°	44.0	30.7	98.7	95	2.88	74 : 26
36 + 37	0.13	NaOD(0.45 M)	CD_3OD	22°	13.7	7.0	39.7	103	3.92	79 : 21
36 + 37	0.17	NaOD(0.45 M)	CD_3OD	22°	44.0	22.0	-	-	4.00	80 : 20
15[f]	-	NaOH(0.46 M)	CH_3OH	0°	14.5	12.0	-	-	2.40	71 : 29
39	0.085	NaOD(0.45 M)	CD_3OD	22°	30.5	26.0	91.0	99	2.35	70 : 30
16	-	$^1O_2$[g]	CH_3OH	15°	24.5	36.0	34.6[h]	81	1.36	58 : 42
16	-	$^1O_2$[g]	CH_3OH	15°	6.0	9.0	24.5[h,j]	85	1.33	57 : 43
16	-	$(C_6H_5O)_3PO_3$	CH_2Cl_2	-70°	6.0	7.0	29.0[h]	80	1.71	63 : 37
16	-	$(C_6H_5O)_3PO_3$	CH_2Cl_2	-70°	5.0	6.7	-	-	1.50	60 : 40

[a]Conditions for each experiment are shown individually in the Table. [b]From n.m.r. integration. [c]Peak at τ 4.40 for 12 and at τ 5.10 for 13. [d]Reference is benzene unless otherwise noted. [e]Yield based on an internal reference and was determined by n.m.r. [f]Preliminary run only, product was isolated by extraction of the reaction mixture with dichloromethane. [g]Generated by photosensitization with methylene blue. [h]Reference is 1,4-dimethoxybenzene. [j]Reference is 0.0030 moles 1,4-dimethoxybenzene. [k]Errors are ± 2%.

The experiments shown were generally carried out at only one concentration of base and substrate since Scott (2) had shown that in the case of 6 the ratio of allylic hydroperoxides formed did not vary with the concentration of base and 6.

Scott (2) had also shown that treatment of either a β-halohydroperoxide or its p-nitrobenzoate ester with base gave identical ratios of allylic hydroperoxides in the product. This was confirmed here since a preliminary reaction of 15 with base gave a ratio of 12 to 13 of 2.4 which is the same as the value for the perester 39 in Table I. Thus, it was concluded that the 12/13 ratios for 11 and 38 were the same (average 12/13 = 2.67).

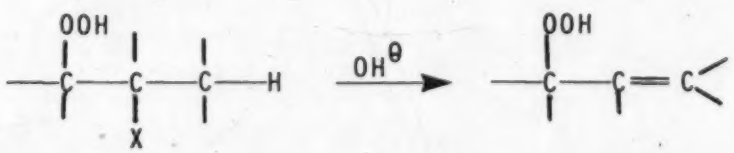
An attempt to directly observe the perepoxide of isopropylidenecyclopentane was made by carrying out the reaction between 11 and base at -60° in the n.m.r. spectrometer. It was hoped that if the reaction was slow enough at this temperature the gem-dimethyl signal of the perepoxide might be observable. However, it appeared that the reaction was complete (only the spectrum of products 12 and 13 was observed) in less than 30 s. The reaction is too fast to observe the perepoxide by this method. van de Sande (1) also could not observe the perepoxide of tetramethylethylene by a similar method.

Table I also gives the results obtained for the production of allylic hydroperoxides from photosensitized

oxidation of 16 and from the reaction of 16 with triphenyl phosphite ozonide (36). As can be seen the results in these two cases are similar, but, as pointed out in the discussion this does not imply a similarity in mechanism.

D I S C U S S I O N

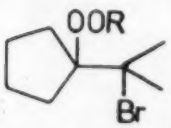
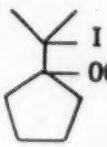
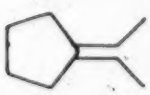
The objectives of the research described in this chapter were to provide more evidence for the intermediacy of a perepoxide in the reaction of β-halohydroperoxides of tetrasubstituted olefins with base and to try to show that a direct elimination pathway to the product allylic hydroperoxides makes only a slight contribution, if any, to the overall reaction. The following discussion will show to what extent these objectives were accomplished. The reaction under consideration is shown below, eq. [13].

[13] 

A summary of the results is found in Table II. In all reactions of either β-halohydroperoxides or their p-nitrobenzoate esters the allylic hydroperoxide with the rearranged hydroperoxy group, 12, was the predominant product. Scott (2) had found in the case of the reaction at base with the β-halohydroperoxides of 18 that the allylic hydroperoxide product ratio 8/9 did not depend on the leaving group. In the case of 16 here, the ratio 12/13 is the same for the iodo and bromo compounds but the results for the chlorohydroper-

TABLE II

Composition of the Allylic Hydroperoxide Mixtures

Reaction	Composition of Product Mixture [a] %12	%13
 + base 11, R = H 38, R = COC_6H_4-p-NO_2	72.5	26.5
Cl, $OOCOC_6H_4$-p-NO_2 + base 36 + 37	79.5	20.5
 I $OOCOC_6H_5$-p-NO_2 + base 39	70.0	30.0
 + $^1O_2$ 16	57.5	42.5
+ $(C_6H_5O)_3PO_3$	61.5	38.5

[a] Values shown are averages of results shown in Table I

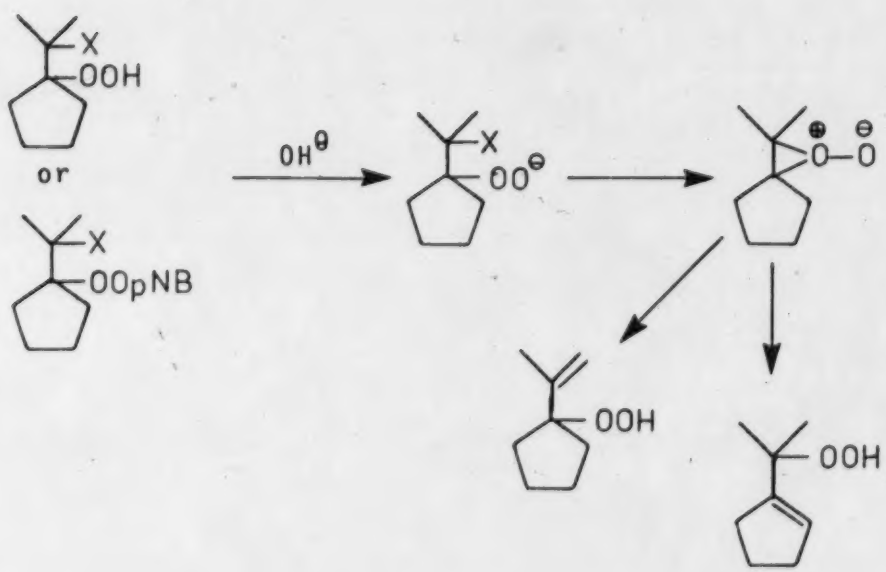
oxide ester seem out of line.

It is important to remember that the ester of the chlorohydroperoxide is actually a mixture of two isomers and that this mixture was shown to be pure by analysis. If it is assumed that the perepoxide mechanism is the correct one, then 36 and 37 should give the same perepoxide as 38 and 39 and, therefore, the same allylic hydroperoxide ratio. This is not observed. Assuming that 36 at least will react with base *via* a perepoxide (its structure is analogous to that of 38 and 39) and knowing that the composition of the chlorohydroperoxide ester mixture is 3:1, then the 36 in the mixture should give 72% 12 and 18% 13 on reaction with base. If this is so, then in order to obtain the observed 12/13 ratio for the 36 + 37 mixture, all the 37 is forced to react *via* a direct elimination pathway. This seems unlikely and something, as yet unknown, must be occurring here.

In the case of the bromo- and iodohydroperoxides and their esters, however, the fact that the 12/13 ratio does not vary with halogen, provides good evidence that these compounds must react only *via* a halogen-free intermediate, the perepoxide, because only a perepoxide intermediate can account for the migration of the hydroperoxy group. This confirms the results of Scott (2), who found no effect of leaving group in the isopropylidenecyclohexane

series. As explained in the introduction van de Sande had also shown that direct elimination was not occurring in his system, eq. [2]. The mechanism for the reaction of base with the bromo- and iodohydroperoxides and esters is presented in Scheme I. The chloro compounds cannot be included here due to the problems already discussed, however, Scott's (2) results imply that they follow the same mechanism.

SCHEME I

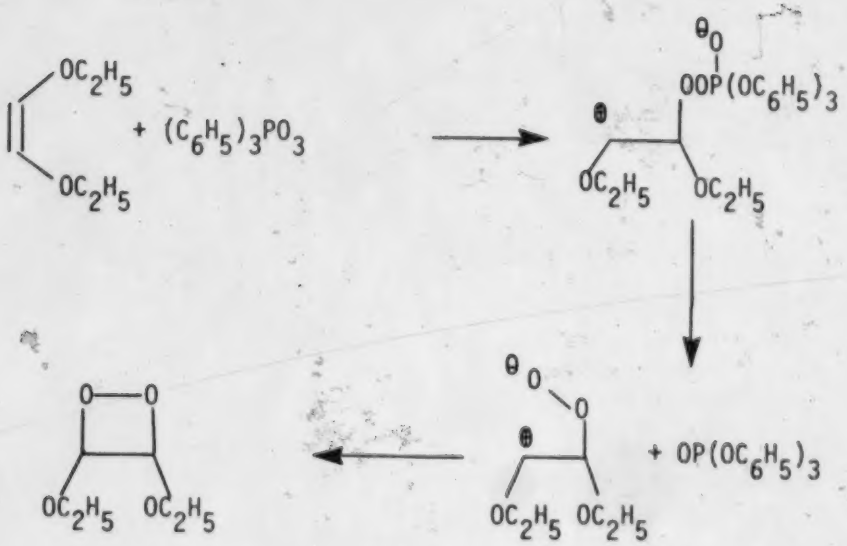


Reactions of 16 with singlet oxygen and with triphenyl phosphite ozonide were carried out for comparison

with the reactions of the β-halohydroperoxides and esters with base. The results obtained are quite different and it appears that neither the reaction of singlet oxygen nor the reaction of triphenyl phosphite ozonide with 16 involve a perepoxide intermediate. This confirms the results of Scott (2) and Kopecky and van de Sande (3) and in the case of the singlet oxygen reaction this conclusion is also in agreement with most of the literature since as discussed in the introduction most authors favour the concerted mechanism of Nickon (17,18) for the addition of singlet oxygen to olefins.

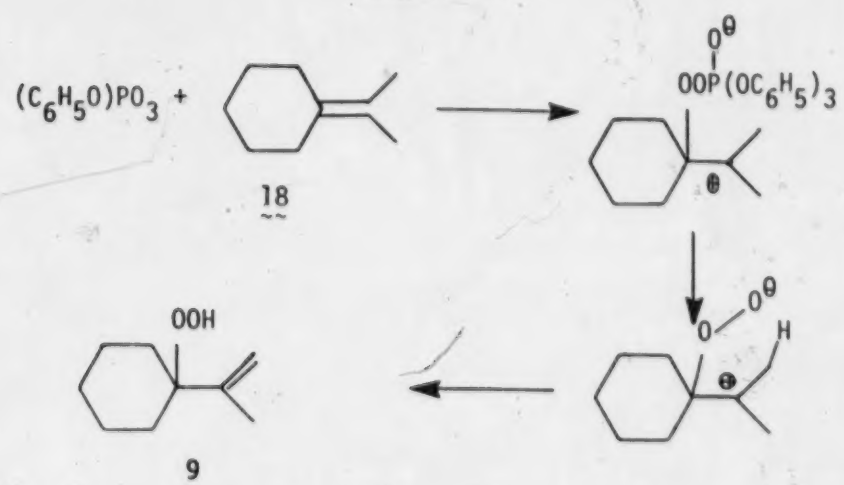
As can be seen in Table II the results obtained from the reaction of 16 with singlet oxygen and triphenyl phosphite ozonide are similar. This is coincidence since Bartlett and Mendenhall (36) have shown that at -70°C, singlet oxygen is not involved in the ozonide reaction although reactions of triphenyl phosphite ozonide mimic two common reactions of singlet oxygen; formation of allylic hydroperoxides (34,35) and formation of dioxetanes (45). Some other mechanism is required to explain the results of the triphenyl phosphite ozonide reaction. Bartlett and Schaap (45) proposed the mechanism shown in Scheme 2 for the formation of dioxetanes from reaction of olefins with triphenyl phosphite ozonide.

SCHEME 2



This mechanism can be adapted to olefins having allylic hydrogens as illustrated for isopropylidenecyclohexane in Scheme 3.

SCHEME 3



18

9

As shown in Scheme 3, this mechanism predicts that only 9 would be formed in the reaction of 18 with triphenyl phosphite ozonide. This conclusion is reached by analogy with the formation of the halohydroperoxides where only 5, 6 and 7 are formed (2). In fact, Scott found that only 9 was formed in the reaction as predicted.

On the same basis treatment of 16 with triphenyl phosphite ozonide should give only 12 as product. However, as can be seen in Table I this is not the case, 12 and 13 being formed in a ratio of 1.60.

Thus the mechanism shown in Scheme 3 cannot be the whole story, at least in the case of 16. It is also difficult to imagine why, if a perepoxide is formed from a β-halohydroperoxide as shown in Scheme 1, one is not formed from the zwitterion shown in Scheme 3. The available data appear to indicate that while the mechanism in Scheme 3 may contribute to the overall reaction it cannot be the whole story. More work is necessary to elucidate the mechanism of the reaction between triphenyl phosphite ozonide and olefins below -40°C.

A logical extension of this work would be to prepare the hydroperoxides 19, 28 and 30 and observe if they give the same product ratios as 11, 14, and 15. This would provide conclusive evidence for a perepoxide intermediate in the reaction of β-halohydroperoxides with base.

EXPERIMENTAL

Melting points and boiling points are reported uncorrected. Refractive indexes were measured using a Bausch and Lomb Abbe-3L Refractometer. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer, ^{1}H n.m.r. spectra were recorded on Varian A-60, A-56/60, HA-100 or Perkin-Elmer R-32 spectrometers. Mass spectral measurements were made on AEI MS-2, MS-9 or MS-12 spectrometers.

Hydrocarbon solvents, Skelly B (hexanes), pentane and isopentane were purified by washing successively with sulphuric acid, water, acidified potassium permanganate solution, water and drying over magnesium sulphate followed by distillation. Anhydrous pyridine was prepared by refluxing reagent-grade material over calcium hydride for several hours followed by distillation from calcium hydride onto activated Type 4A molecular sieves.

The photooxygenation apparatus has been described by van de Sande (1) and was used without modification. Iodometric titrations were carried out using the method of Organic Synthesis (45). Drying of solutions was done with magnesium sulphate unless otherwise stated. Concentration of solutions was carried out on a Buchi rotary evaporator using a dry-ice condenser and a bath at room temperature unless otherwise noted.

1-(Methylvinyl)cyclopentanol, 27:

The Grignard reagent was prepared from purified 2-bromopropene following the method of House (47).

To magnesium turnings (14.6 g, 0.6 moles) and tetrahydrofuran (400 ml) in a 1 liter, three-necked flask equipped with a reflux condenser, a mechanical stirrer and a pressure-equalized dropping funnel was added a few ml of 2-bromopropene and a crystal of iodine. The reaction was started by crushing a few pieces of magnesium and 2-bromopropene (72.6 g, 0.6 moles) in tetrahydrofuran (150 ml) was added dropwise so as to maintain the solvent at reflux. After the addition was complete the reaction mixture was refluxed 0.5 h.

To this solution of the Grignard reagent a solution of cyclopentanone (50.4 g, 0.6 moles) in tetrahydrofuran (50 ml) was added dropwise. When the addition was complete the reaction mixture was refluxed 0.5 h.

Saturated aqueous ammonium chloride solution was added dropwise with vigorous stirring until the precipitated salts became granular. The clear supernatant was then decanted and the salts extracted exhaustively with ether. The combined organic layers were washed with water (3 x 200 ml), dried and concentrated to an oil. Residual solvent was removed by distillation at atmospheric pressure and the residue was distilled to yield 34.0 g (45%) of a clear

colourless product, b.p. 68 - 70°C (15 torr), $n_D^{23.5}$ 1.4752; reported b.p. 72 - 75°C (18 torr), $n_D^{26.5}$ 1.4745 (2).

The i.r. spectrum (neat) showed absorptions at 3380 (OH stretch) and 1645 cm^{-1} (C=C stretch).

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 4.97 (m) and τ 5.20 (m) for the olefinic protons, τ 7.70 (s) for the OH proton and τ 8.25 (broad) for the remaining protons in a ratio of 1 : 1 : 1 : 11 as required.

Isopropylidenecyclopentane, 16:

This procedure was adapted from that of Birch (48).

A solution of sodium (10.95 g, 0.476 moles) in liquid ammonia (350 ml) was prepared in a 1 liter, three-necked flask equipped with a dry-ice condenser, a pressure equalized dropping funnel and a magnetic stirrer. A solution of 27 (30 g, 0.238 moles) in 98% ethanol (12 g) and ether (70 ml) was added dropwise with vigorous stirring. When the addition was complete, 98% ethanol (12 g) was added and the solution was refluxed 2 h. Just enough water was added to discharge the remaining blue colour, the condenser was removed and the ammonia was allowed to evaporate overnight.

The residue was dissolved in water (150 ml) and the solution was extracted with ether (4 x 100 ml). The combined ether extracts were washed with water until

neutral, dried and concentrated to an oil by distillation at atmospheric pressure. The residue was absorbed into glass wool and distilled to yield a clear colourless liquid, b.p. 38°C (12 torr), yield 16.9 g (65.5%), n_D^{23} 1.4570; reported (37) b.p. 135.5 - 137.5°, n_D^{20} 1.4585.

The i.r. spectrum (neat) showed absorptions at 2950 (C-H stretch) and 1647 cm^{-1} (C=C stretch).

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 7.83 (broad) and τ 8.39 (broad) in a ratio of 1 : 2.6; required 1 : 2.5.

1-(1-Bromo-1-methylethyl)cyclopentyl hydroperoxide, 11:

To a 250 ml, three-necked flask equipped with a drying tube, a cold bath at -40°, a magnetic stirrer and a low temperature thermometer was added ether (30 ml) and 98% hydrogen peroxide (8.5 g). When the internal temperature had returned to -40°C, 16 (5.51 g, 0.04 moles) was added. 1,3-Dibromo-5,5-dimethyl hydantoin (7.25 g, 0.025 moles) was added at -40°C in four portions, allowing the reaction mixture to warm to -30°C between additions and to remain at -30°C until most of the hydantoin had dissolved. Then the reaction mixture was cooled to -40°C and another portion of hydantoin was added. When most of the final portion of hydantoin had dissolved the reaction

temperature was allowed to rise slowly to -15°C and then The reaction mixture was poured into ice-water (30 ml). The organic layer was washed with ice-water (30 ml), ice-cold aqueous 10% sodium thiosulphate solution (30 ml), ice-water (2 x 30 ml) and dried at 0°C. The solution was concentrated to an oil on the rotary evaporator using a bath at 0°C. This crude oil must not be allowed to warm above 0°C since the partial decomposition resulting prevents further purification.

The crude material was purified by recrystallization (3x) from isopentane at -78°C. The product was a white solid, m.p. -10°C to -5°C, 99.2% pure by iodometric titration, yield 4.4 g (38%).

The i.r. spectrum (neat) shows absorption at 3340 cm^{-1} (O-H stretch).

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 2.40 (broad, OOH), τ 8.12 (s, methyl groups) and τ 8.0 (broad, ring protons).

1-Hydroperoxy-1-(1-bromo-1-methylethyl)cyclopentyl p-nitrobenzoate, 38:

11 (0.58 g, 0.0026 moles) was dissolved in anhydrous pyridine (3.5 ml) and p-nitrobenzoyl chloride (0.5 g, 0.0026 moles) was added. The reaction mixture was stirred 15 m and then diluted with water (25 ml). This solution

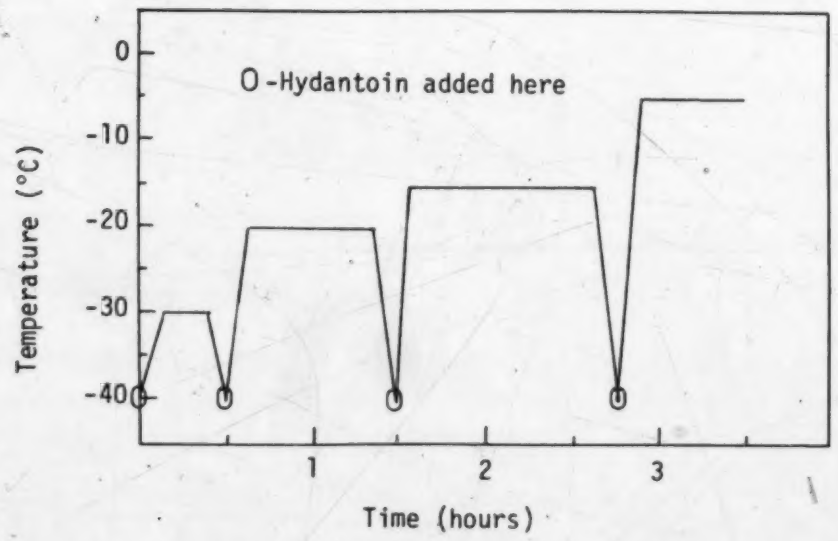
was extracted with ether (2 x 20 ml) and the combined organic solutions were washed with 5% aqueous sodium carbonate solution (2 x 20 ml), 5% aqueous copper (II) sulphate solution until all the pyridine was removed, water (2 x 20 ml) and dried. Removal of the solvent gave 38 as a white powder. This was recrystallized from ether-pentane (3x) at -20°C to yield a faintly yellow crystalline solid, 0.78 g (80%), m.p. 94 - 96 (decomp).

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 1.75 (q, aromatic hydrogens), τ 8.04 (s, methyl hydrogens) and τ 7.6 - 8.4 (broad, ring hydrogens). The relative areas of the aromatic signals to the combined aliphatic signals was 1 : 3.5 as required.

Analysis : Calculated for $C_{15}H_{18}NO_5Br$: C, 48.40; H, 4.87; N, 3.76; Br, 21.47; Found : C, 48.14; H, 4.81; N, 3.70; Br, 21.49.

Preparation of the Chlorohydroperoxides of 16; 14 and 28:

This preparation was done using the procedure used for the synthesis of 11. The reagents were ether (25 ml), 98% hydrogen peroxide (7.72 g) and 16 (5.0 g, 0.045 moles). 1,3-Dichloro-5,5-dimethylhydantoin (4.47 g) was added in four portions as shown by the following graph:



When all the hydantoin had dissolved, the reaction mixture was worked up as before. The product was a colourless oil, yield 6.4 g (79%). Attempts to purify the crude hydroperoxide by crystallization and low temperature chromatography gave products that were only 83% pure by iodometric titration.

The n.m.r. spectrum of the crude material showed absorptions at τ 3.10 (s, OOH), τ 8.33 (s, gem-dimethyl group of 14), τ 8.54 (s, gem-dimethyl group of 28) and τ 8.2 (broad, ring hydrogens).

Preparation of the p-Nitrobenzoate Esters of 14 and 28, 36 and 37:

The crude chlorohydroperoxide mixture prepared above (5 g, 0.028 moles) was dissolved in anhydrous pyridine (3.5 ml) and p-nitrobenzoyl chloride (5 g, 0.026 moles)

was added. After a few minutes a precipitate formed and the reaction mixture was allowed to stand for 15 m. It was then diluted with water (30 ml) and the oily solid formed was washed with 5% aqueous sodium carbonate solution (2 x 20 ml). The remaining solid residue was dissolved in ether (40 ml) and this solution was washed with 5% aqueous copper (II) sulphate solution (20 ml), water (10 ml) and dried. Removal of the solvent gave a yellow solid which was recrystallized (3x) from Skelly B to give light yellow crystals, yield 1.75 g, m.p. 71 - 75°C.

The perester was purified by column chromatography at -40°C on Silica gel (20 g) using Skelly B : ether :: 4 : 1 as the eluant. Recovery from the column was 50% of a mixture of 36 + 37, m.p. 73 - 75°C.

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 1.71 (q, aromatic), τ 8.21 (s, gem-dimethyl of 36), τ 8.36 (s, gem-dimethyl of 37) and τ 8.0 (broad, ring hydrogens of both isomers). The relative areas of the aromatic signals to all aliphatic signals was 1 : 3.4, required 1 : 3.5.

Analysis: Calculated for $C_{15}H_{18}ClNO_5$: C, 54.97; H, 5.54; N, 4.27; and Cl, 10.81. Found: C, 54.96; H, 5.61; N, 3.98; and Cl, 11.07.

1-(1-Iodo-1-methylethyl)cyclopentyl hydroperoxide, 15:

DANGER - PURE MATERIAL EXPLODES VIOLENTLY

The procedure used in the preparation of 11 was followed using ether (25 ml), 98% hydrogen peroxide (4.25 g) and 16 (2.76 g, 0.025 moles). 1,3-Diiodo-5,5-dimethylhydantoin (4.79 g, 0.0125 moles) was added over 40 m while maintaining the reaction mixture between -30°C and -40°C. The product was a colourless oil, 5.2 g (77%), 86% pure by iodometric titration. The material could be purified by low temperature column chromatograph (-40°C) on Silica gel using Skelly B : ether :: 4 : 1 as the eluant, to give a colorless oil, 98% pure by iodometric titration. Removal of the solvent at -20° using a vacuum pump gave a colourless oil which exploded on warming.

The n.m.r. spectrum ($CDCl_3$) at -30°C showed absorptions at τ 0.46 (s, OOH), τ 7.94 (s, methyl groups) and τ 8.25 (broad, ring protons). The ratio of the areas of the hydroperoxy signal to the aliphatic signals was 1 : 21, required 1 : 15.

1-Hydroperoxy-1-(1-iodo-1-methylethyl)cyclopentyl p-nitrobenzoate, 39:

Crude 15 (0.675 g, 0.0025 moles) was dissolved in anhydrous pyridine (3 ml) at 0°C and p-nitrobenzoyl chlor-

ide (0.464 g, 0.0025 moles) was added with stirring. The solution was stirred 5 m at 0°C and 10 m at 22°C. Water was added and the precipitate was washed successively with water (2 x 10 ml), saturated aqueous sodium carbonate solution (2 x 10 ml) and water (10 ml). The solid was collected by filtration, yield 0.7 g.

The yellow solid was purified by low temperature chromatography (-40°C) on Silica gel (20 g) using Skelly B : ether :: 4 : 1 as the eluant. The sample was applied to the column in toluene. Fractions from the column, containing the product were concentrated to one-half volume, Skelly B (30 ml) was added and the solution was cooled to -78°C. The yellowish crystals of 39 were collected and recrystallized from ether/Skelly B, to yield 0.3 g (27%) of yellowish crystals which decomposed without melting at 75 - 80°C.

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 1.76 (q, aromatic), τ 7.86 (s, methyl groups) and τ 8.0 (broad, ring protons). The relative areas of the aromatic signals to the aliphatic signals were in a ratio of 1 : 3.7, required 1 : 3.5.

Analysis: Calculated for $C_{15}H_{18}INO_5$: C, 42.97; H, 4.33; N, 3.34 and I, 30.27. Found: C, 43.24; H, 4.23; N, 3.17 and I, 30.20.

Reaction of 11 with Base:

A solution of 11 (0.08756 g, 3.92×10^{-4} moles) and benzene (0.01097 g, 1.40×10^{-4} moles) in perdeuterated methanol was made up to exactly 1.0 ml. A second solution of sodium (0.0397 g, 1.73×10^{-3} moles) and deuterium oxide (0.0612 g, 3.06×10^{-3} moles) in perdeuterated methanol was made up to exactly 2.0 ml. Equal volumes of these solutions were mixed in an n.m.r. tube at 20°C and the spectrum was observed immediately. When the spectrum was analyzed using benzene as the internal reference, it was found that 11 had been converted to 12 and 13 in 100% yield.

The n.m.r. spectrum at 15°C showed absorptions at τ 2.68 (s) for the benzene reference, τ 4.44 (t) for the olefinic proton of 12, τ 4.85 (s) for HOD, τ 5.10 (m) for the olefinic protons of 13, τ 6.70 (m) for solvent methanol, τ 7.66 (broad) and τ 8.2 (broad) for the ring protons of 12 and 13 and τ 8.68 (s) for the gem-dimethyl protons of 12. The areas of the required signals are shown in Table I.

Reaction of 11 with Base at -60°C:

A cold (-60°C) 0.42 M solution of 11 in methanol was mixed with an equal volume of a cold (-60°C) methanol solution, 1.13 M in sodium hydroxide and 0.40 M in ani-

sole (as internal standard) in an n.m.r. tube at -60°C. The tube was placed in the cold (-60°C) probe of an n.m.r. spectrometer and the region τ 1.0 to τ 2.0 was rapidly (scan complete about 30 s after mixing) scanned. The spectrum showed only one gem-dimethyl singlet at τ 8.32 due to 12. No trace of the gem-dimethyl signal of 11 was observed.

Reaction of 36 + 37 with Base:

A solution of sodium (0.0413 g, 1.80×10^{-3} moles), deuterium oxide (0.0457 g, 2.23×10^{-3} moles) and benzene (0.01652 g, 2.11×10^{-4} moles) in perdueterated methanol was made up to exactly 2.0 ml with perdeuterated methanol.

The solution for analyses was prepared in the following manner, since the peresters were not soluble in methanol. 36 + 32 (0.0264 g, 8.05×10^{-5} moles) was divided into four portions. One portion was added to perdeuterated methanol (0.30 ml) and the prepared base solution (0.025 ml) was added. When the perester had dissolved, a second portion was added followed by base (0.025 ml). This procedure was repeated until all the perester had been used. The last addition of base was 0.225 ml. When analyzed by n.m.r. spectroscopy quantitative conversion of 36 + 37 to 12 and 13 was observed.

The n.m.r. spectrum at 15°C was essentially the

same as that described for the reaction of 11 with base. The areas of the required signals are shown in Table I.

Reaction of 39 with Base:

This was done exactly as for the reaction of 36 + 37 above, using the same base solution and 39 (0.0430 g, 1.03×10^{-4} moles). Quantitative conversion of 39 to 12 and 13 was observed by n.m.r. spectroscopy.

The n.m.r. spectrum at 15°C was essentially the same as that described for the reaction of 11 with base. Integration of the required signals is shown in Table I.

Reaction of 38 with Base:

This was carried out as described in the reaction 36 + 37 with base but using 38 (0.0450 g, 1.21×10^{-4} moles) and a base solution composed of sodium (0.03540 g, 1.54×10^{-3} moles), deuterium oxide (0.05895 g, 2.95×10^{-3} moles) and benzene (0.01607 g, 2.13×10^{-4} moles) made up to exactly 2.0 ml with perdeuterated methanol.

The n.m.r. spectrum at 15°C was essentially the same as that described for the reaction of 11 with base. The areas of the required signals are shown in Table I.

Photosensitized Oxygenation of 16:

A solution of 16 (1.0 g, 0.009 moles), 2,6-di-t-butylphenol (0.1 g), 1,4-dimethoxybenzene (0.1380 g)

and methylene blue (0.050 g) in methanol (30 ml) was photooxygenated for 65 m after which time 120% of the theoretical volume of oxygen had been consumed. The reaction mixture was poured into water (75 ml) and extracted with ether (3 x 50 ml). The combined ether extracts were washed successively with water (50 ml), saturated aqueous sodium chloride solution (50 ml) and dried. Concentration gave a colourless oil, 82% yield by n.m.r.

The n.m.r. spectrum ($CDCl_3$) was essentially the same as that for the reaction of 11 with base. Of course the signals for benzene, methanol and HOD were missing and signals at τ 3.15 and τ 6.16 for dimethoxybenzene were present. The areas for the required signals are given in Table I.

Reaction of 16 with Triphenyl Phosphite Ozonide:

This procedure was based on that of Bartlett and Mendenhall (36) and Scott (2).

An ozone-free solution of triphenyl phosphite ozonide in dichloromethane (25 ml) at -78°C was prepared from triphenyl phosphite (1.4 g, 0.0045 moles). To this solution at -78° was added cold (-10°C) 16 (0.5 g, 0.0045 moles) and the reaction mixture was allowed to stand 12 h at -78°C. This reaction mixture was then warmed to

room temperature and the solvent was removed by vacuum distillation at -35°C, cooling the receiver to -78°C. The residue from the distillation was a colourless oil (3.15 g). The distillate was found to contain 180 mg of 16 that had not reacted. The crude residue was analyzed by n.m.r. spectroscopy ($CDCl_3$) using p-dimethoxybenzene as an internal standard. Taking recovered starting material into account, the yield of allylic hydroperoxides by n.m.r. was 80%.

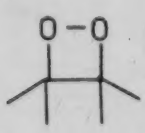
The n.m.r. spectrum ($CDCl_3$) was essentially the same as that reported for the reaction of 11 with base. Of course the signals for benzene, solvent and HOD were missing and signals at τ 3.17 and τ 6.28 for dimethoxybenzene and at τ 2.73 for triphenyl phosphite were present. The areas of the required signals are given in Table I.

CHAPTER II

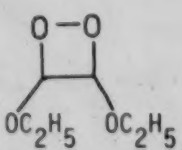
Studies on Tricyclic Dioxetanes

I N T R O D U C T I O N

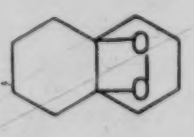
Since the first dioxetane, trimethyl-1,2-dioxetane, was synthesized and characterized by Kopecky and Mumford (49), many new dioxetanes have been prepared and studied. Dioxetanes of widely varying structure have been reported, for instance, tetramethyl-1,2-dioxetane (5), 40, 3,4-diethoxy-1,2-dioxetane (50), 41, the highly strained dioxetane, 21, from adamantylidene adamantane (51) and the tricyclic dioxetane of Filby (38), 11,12-dioxa[4.4.2] propellane, 42. Recently Wynberg (52) has reported an optically active derivative of dioxetane, 21, and Bogan (53) has given indirect evidence for the existence of dioxetane, 43, itself.



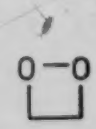
40



41

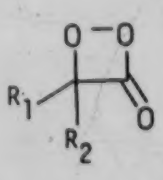


42



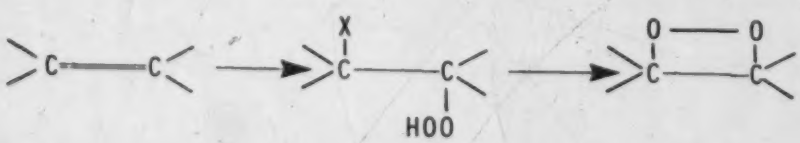
43

As well as the dioxetanes themselves, several 1,2-dioxetanones of the general structure shown below have been prepared and characterized in solution (54-56).



Wilson has recently published a review (57) on dioxetanes which contains a list of all dioxetanes that had been prepared and either fully or partially characterized up to 1975.

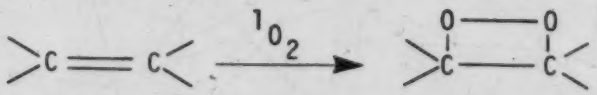
Dioxetanes have been synthesized by two major routes. The first is the β-halohydroperoxide route of Kopecky and Mumford (5,49) in which an olefin is first converted to a β-halohydroperoxide (as described in Chapter I) and the halohydroperoxide is treated either with base for non-tetrasubstituted halohydroperoxides (5,49,58,59) or with silver acetate for tetrasubstituted halohydroperoxides (5,38). The reaction is outlined in eq. [14]. This procedure gives

[14] 

yields of 5-30%.

The second route to dioxetanes involves the 1,2-addition of singlet oxygen to certain electron-rich olefins as outlined in eq. [15]. This reaction only takes place, however, with olefins in which the "ene" reaction to form allylic hydroperoxides (see Chapter I) does not take place either due to the absence of allylic hydrogens (60,61) or to steric restraints (22,51). The singlet oxygen necessary in this reaction has been obtained from either dye-photosensitization (51) or from the decomposition of triphenyl-

phosphite ozonide (45).

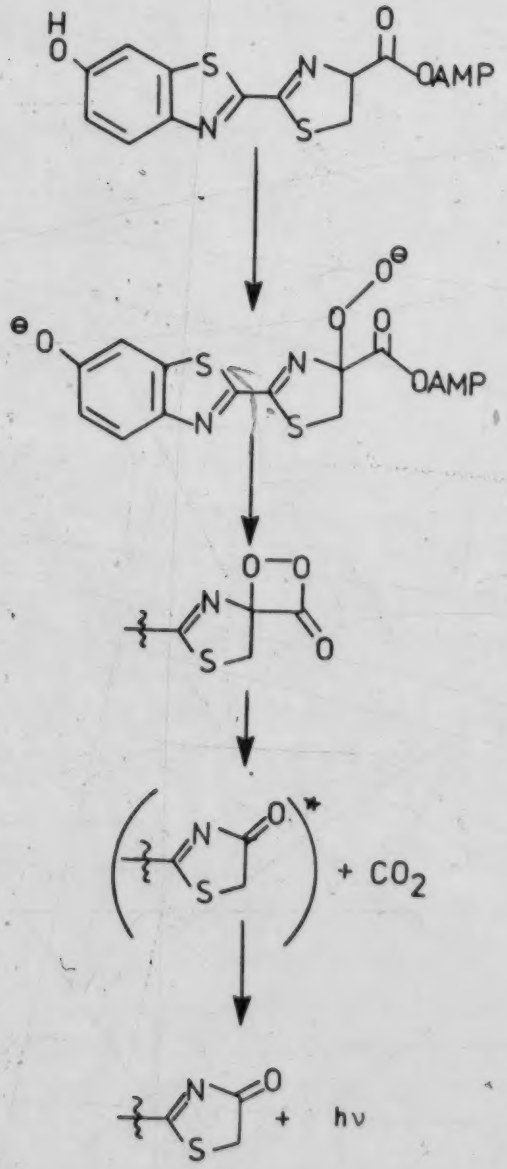
[15] 

Story (62) had reported a synthesis of dioxetanes by ozonation of olefins in pinacolone but this route was shown to be incorrect by Kopecky (41) and Bailey (63).

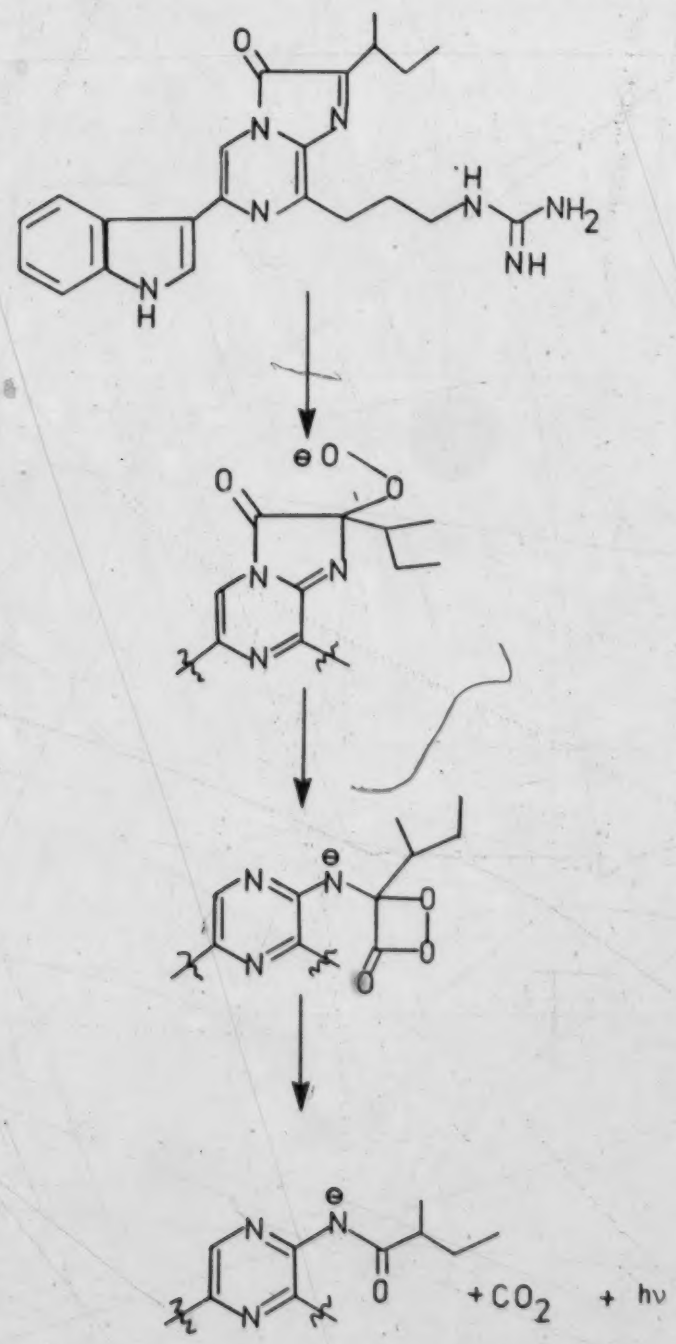
Reactions of dioxetanes with various reagents have been studied (5,64-68) but the most important and most investigated reaction is that on warming dioxetanes are quantatively converted to carbonyl compounds with the emission of light. This observed luminescence implies that electronically excited molecules are being generated from a starting material in its ground state.

The isolation of the first dioxetane (49) and the discovery that it gave off light on heating confirmed McCapra's prediction (69) that dioxetanes would be chemiluminescent. Dioxetanes and dioxetanones had also been proposed (69) as the reactive intermediates in some bioluminescences and in at least two cases, the fire-fly Photinius (70) and the shrimp Cypridina (71), dioxetanones have been conclusively implicated in bioluminescence (72). Scheme 4 shows the proposed mechanism of bioluminescence of Photinius and Scheme 5 that of Cypridina.

SCHEME 4



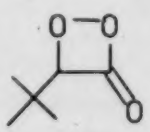
SCHEME 5



As well as explaining some bioluminescences it was hoped that study of dioxetane chemiluminescence would lead to a better understanding of energy transfer processes and excitation processes as well as chemiluminescence itself.

In order to learn more about the mechanism of dioxetane decomposition and the processes involved, the rates of reaction, activation parameters, and yields and identities of the excited states had to be found.

The rates of decomposition of dioxetanes can be followed by iodimetry or by n.m.r. (5,38) or by the decay of chemiluminescence in the presence of a fluorescer (50) as used in this research. The first order rate constants range from about 10^{-3} s^{-1} at 22°C for the unstable 1,2-dioxetanones such as 44 (55) to 7×10^{-5} s^{-1} at 142°C for the stable dioxetane 21 (73).



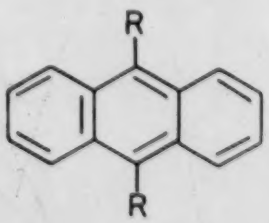
44

The activation parameters can be determined either from the temperature dependence of the rate constants in the traditional way, (Arrhenius plots) or by a clever method developed and used by Wilson (50,74). Both methods are used in the research that follows and they are fully described in the Results section.

Activation parameters and rate constants provide some information, but since thermolysis of dioxetanes produces excited states it is important to determine which excited species are being produced and what is the efficiency of their production. Before discussing excited state counting methods more information about dioxetane thermolysis is required. Kopecky and Mumford (49) showed that both singlet and triplet species were present in the thermolysis of trimethyl-1,2-dioxetane. White (75,76) suggested for trimethyl-1,2-dioxetane and Turro (77) showed for tetramethyl-1,2-dioxetane that both singlet and triplet ketones are generated directly from the dioxetane. This has been confirmed by Wilson (50). O'Neal and Richardson (78,79) have calculated that in dioxetane thermolysis enough energy is released to excite only one of the product carbonyl groups to either its singlet or triplet state. These calculations were confirmed by Turro (80,81) who found that the transition state for the disappearance of dioxetane, 40, was higher in energy than both the singlet and triplet states of acetone.

The method used in this research for determining the yields of excited states is due to Wilson (50), who has used it successfully in several cases (50,74,82), as has Filby (38). Wilson observed that the chemiluminescence intensity using the fluorescer 9,10-dibromoanthracene, DBA, 45, was considerably greater than when 9,10-diphenylanthracene, DPA,

46, was used. This was somewhat unusual since DPA is a much more efficient fluorescer than DBA (83). However, due to the heavy atom effect, DBA is capable of converting triplet energy to singlet energy much more efficiently than DPA (84). Consideration of these two facts leads to the inevitable conclusion that much more triplet excited state product is formed on dioxetane thermolysis than singlet excited product. Wilson developed this observation into a method to count excited singlet product using DPA and excited triplet product with DBA. This method is discussed operationally in the Results section. Other authors (56,75,77,85-91) have used different methods to count excited products and these have been recently reviewed by Wilson (57). Note that where the chemiluminescence methods and other methods have been applied to the same compound the results are generally very comparable.



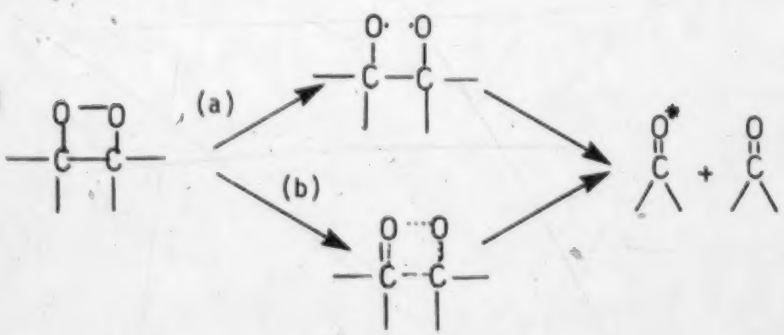
46, R = C_6H_5

45, R = Br

The general result of all these counting procedures is that triplet yields (0.1 to 0.3) are larger by at least

two orders of magnitude than singlet yields. Any mechanism proposed for the thermolysis of dioxetanes must explain this fact.

The mechanism of the thermal decomposition of dioxetanes is a matter of considerable importance and also of considerable controversy. Two extreme possibilities for the mechanism have been discussed and are shown in eq. [16].

[16] 

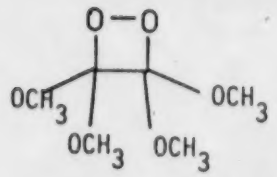
Path (a) is the biradical mechanism proposed by Richardson (59,78,89) and path (b) is the concerted mechanism suggested first by McCapra (69) and supported by Kearns (92).

Kearns (92) has shown that the concerted mechanism can explain the high yield of triplet product and Richardson (89) has shown that the biradical mechanism can also account for it. Both mechanisms have been discussed thoroughly by Wilson (57) and this comparison will not be repeated here. As yet the exact mechanism of dioxetane thermolysis is unknown but it may well turn out to be a mechanism such as that proposed by Turro (81) in which the O-O bond is considerably stretched before simultaneous

breaking of the O-O and C-C bonds occurs (this is the so-called "nearly-concerted" mechanism).

One important feature of the biradical mechanism is that it can predict quite accurately the activation parameters for thermolysis of dioxetanes. Richardson has shown that by using the group additivity method of Benson (93-95) the activation parameters of several dioxetanes could be calculated and that the calculated values agreed with the experimental data (78,79,89,96).

In view of the number of dioxetanes that have been well characterized it would not be surprising to find some correlation between dioxetane structure and the production of excited states. No such correlation appears to exist (82,97). The activation energies of most dioxetanes are 25 ± 2 kcal mole^{-1} and the singlet and triplet yields lie between 10^{-4} to 10^{-2} and 0.1 to 0.5, respectively. Amid this frustrating regularity, there are but few exceptions. 21 has an activation energy of about 35 kcal mole^{-1}, but this can be attributed to steric effects operating in a biradical or biradical-like mechanism. Only two other exceptions stand out since Wilson (82) has shown that the work of Darling and Foote (86,87) on 3,4-di-n-butyl-3,4-dimethyl-1,2-dioxetane (they obtained higher singlet than triplet yields) was incorrect. These exceptions are tetramethoxy-1,2-dioxetane (74), 47, and 42.



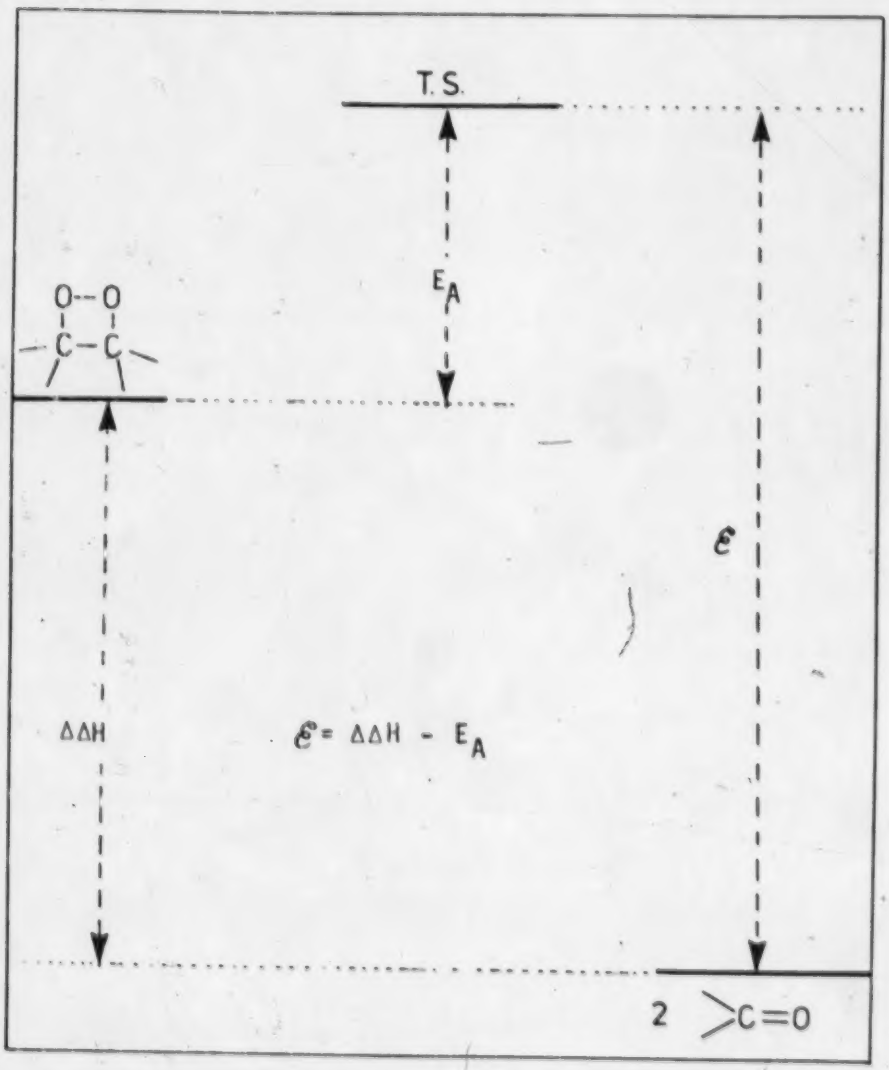
47

47 has an activation energy of 28.6 kcal $mole^{-1}$ and a singlet yield of 0.01 and a triplet yield of 0.1. 42 has an activation energy of 22.7 kcal $mole^{-1}$ and $^1\phi < 10^{-5}$ and $^3\phi = 8 \times 10^{-3}$.

Before we can begin to understand the factors affecting the yields of excited states we must first know where the energy of excitation comes from. It can be seen in Figure 1 that the energy available for excitation of the product is equal to the difference between the heats of formation of reactant and products plus the activation energy. Perrin (98) has challenged this scheme on thermodynamic grounds but Lissi (99) and Wilson (100) have both shown on a theoretical basis that Perrin is not correct. We shall see that this work and the work of Filby (38) provide experimental evidence to counter Perrin's suggestions and further discussion is left until later.

FIGURE 1

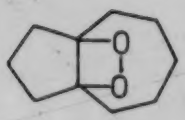
Energy Available ($\mathcal{E}$) from Decomposition of 1,2-Dioxetanes



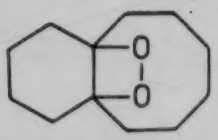
The research described in this chapter was started as a direct result of the work of Filby (38) on 42. Although dioxetane structure generally appears to have little effect on the yields of excited states and activation parameters, the tricyclic structure of 42 was quite different from other dioxetanes and deserved further study. The questions to be answered were, does the tricyclic nature of 42 cause the low triplet yield and if so, how? Also, do all tricyclic dioxetanes behave in the same fashion? Filby (38) had suggested that strain in the product diketone from 42 might cause a low triplet yield by reducing the energy available on thermolysis. This suggestion of Filby's is discussed in detail in the Discussion in the light of the results obtained from this research.

In order to answer these questions it was decided to prepare the series of tricyclic dioxetanes shown below, 9,10-dioxa[3.3.2]propellane, 48; 11,12-dioxa[5.3.2]-propellane, 49; and 13,14-dioxa[6.4.2]propellane, 50. The products of thermolysis of 48, 49 and 50 would be the cyclic diones 51, 52 and 53. The following chapter deals with the synthesis and study of 48, 49 and 50.

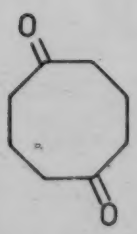
48



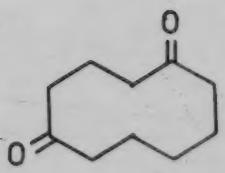
49



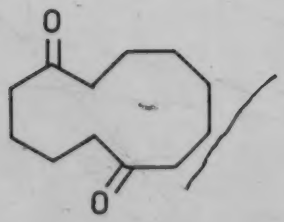
50



51



52



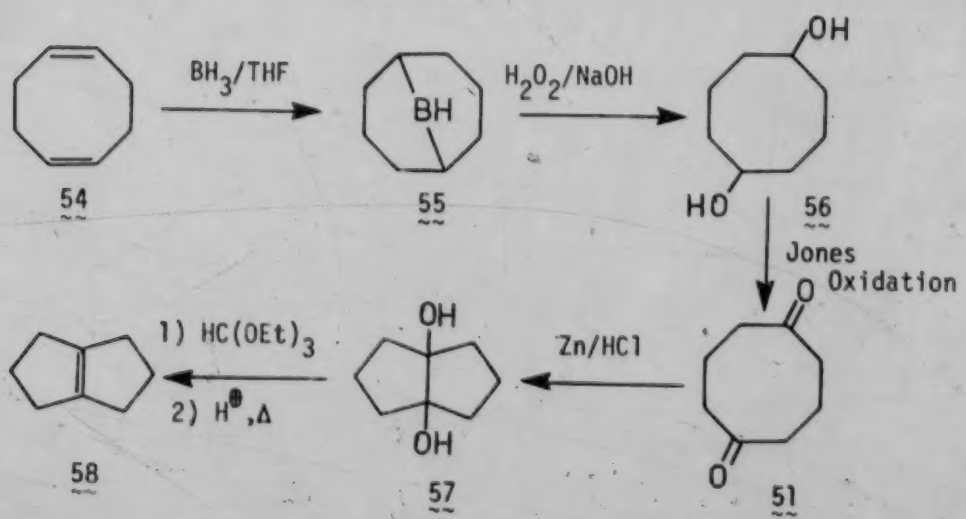
53

RESULTS

Preparation of 1(5)-Bicyclo[3.3.0]octene, 58:

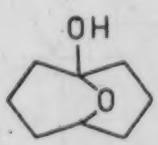
The route chosen to the title compound is shown in Scheme 6.

SCHEME 6



The olefin, 58, has been prepared by many authors in various ways (101-106) but no one has bettered the 22% yield obtained here. The worst step, the Jones oxidation, resulted in only 33% yield. Among the drawbacks of earlier preparations of 58, was that many required alkyl lithiums which are expensive and also pose handling problems for the occassional user. In Scheme 6 only the first step must be carried out in an inert atmosphere and this may be avoided since 55 is commercially available as a dry powder which is not air-sensitive (107).

The preparation of the dione, 51, was adapted from Alvik (108). Initial oxidation of 56 with Jones reagent gave the hemiacetal, 59, which was identified by comparison with an authentic sample (109,110). Reoxidation of the hemiacetal with Jones reagent gave the dione, 51, but at a much slower rate than the oxidation of 56 to 59.

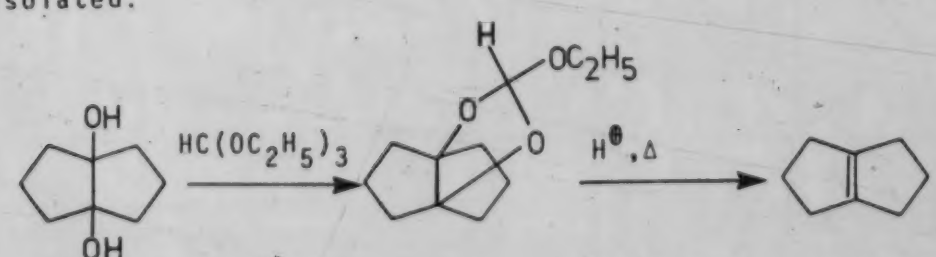


59

57 was prepared as suggested by Borden (101) using the procedure of Wenkert (111). The best yields of 57 were obtained when the reaction was carried out on the scale given in the Experimental section since in larger quantities the zinc amalgam cannot be efficiently agitated.

The last step shown in Scheme 6 was actually carried out in two steps as shown in eq. [17] since the best yield of olefin was obtained when the intermediate orthoester was isolated.

[17]



57 60 58

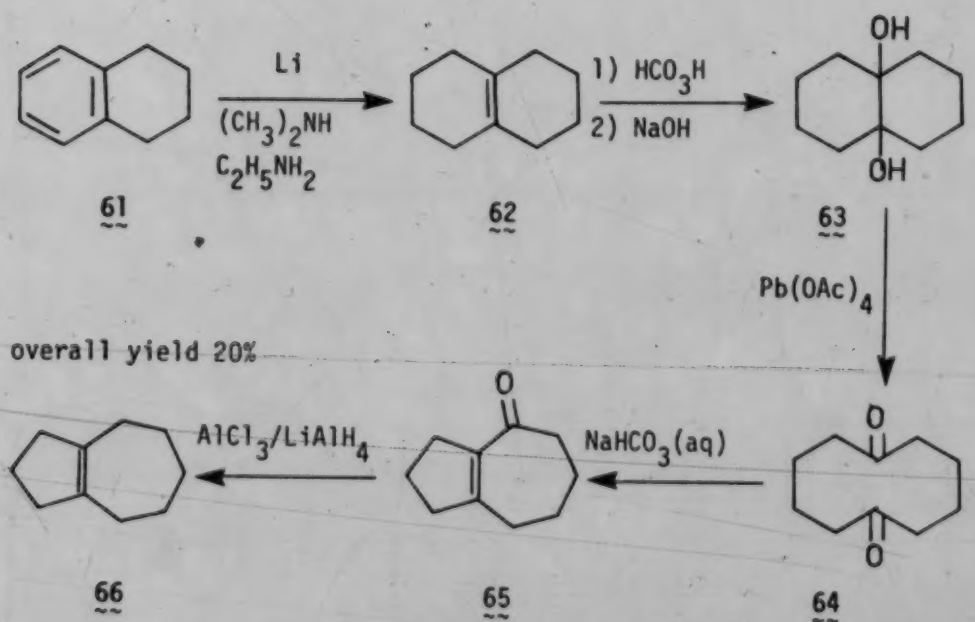
This method was introduced by Eastwood (112-114). This reaction gave very poor yields until a batch of 57 that had been recrystallized from carbon tetrachloride was used. The conversion of 57 to 60 requires a trace of acid catalyst and presumably some traces of HCl from the carbon tetrachloride adhere to the crystals of 57 and catalyze the reaction. 60 was isolated and purified by distillation but it was not fully characterized.

All compounds shown in Scheme 6 were known and had physical constants in agreement with published values.

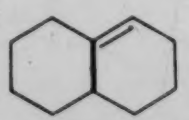
Preparation of 1(7)-Bicyclo[5.3.0]decene, 66:

The route chosen to this olefin is shown in Scheme 7.

SCHEME 7



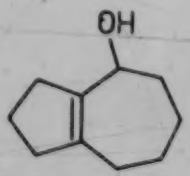
The first step was a modification of the procedure of Benkeser (115) due to Filby (38) and actually resulted in a mixture of 62 and 67 in ratio of 3:1. Although it was possible to obtain pure 62 (115), the use of the mixture to obtain 63 proved satisfactory here.



67

The conversions of 62 + 67 to 63 and 63 to 64 were carried out by the method of Dev (116) and Filby (38), the yield of 64 from 62 + 67 being 66%. Previously, Anderson (117) had produced 64 in only 45% yield by ozonolysis of a mixture of octalins.

Conversion of 64 to 65 was accomplished by the method of Anderson (117) and Cope (118). The mild conditions employed here (aq. $NaHCO_3$) were found to be much more successful than the method of Dev (116) (refluxing HCOOH). 65 appeared to decompose on standing even at -20° so that unless it was to be used immediately it was converted to 68 (117).



68

Initial attempts to prepare 66 from 68 by the same method as used for the preparation of isopropylidenecyclopentane, 16, (reduction with sodium in liquid ammonia) gave low yields. Some other method of preparing 66 had to be found. The method of Brown (119,120) was used although great care was needed in order to prevent rapid decomposition of the reaction mixture. Either 65 or 68 could be used in this reduction with no effect on the product. The material obtained from this reaction was quite impure but 66 could be obtained by column chromatography on either alumina or silica gel using pentane as the eluant.

The olefin 66 had been previously obtained by Kovats, Fürst, and Günthard (121) who had separated it by distillation from a mixture of isomeric compounds. However, it was inadequately characterized (reported only refractive index, boiling point and elemental analysis). Arnold (127) also prepared the olefin but reported only an elemental analyses and a boiling point.

In this research the data presented allow the structure of 66 to be assigned unambiguously. The ^{1}H n.m.r. spectrum shows no signals in the olefinic region indicating that the double bond is tetrasubstituted. Analysis and exact mass measurement of the parent ion in the mass spectrum confirms the elemental composition and purity. The structure proof relies on the ^{13}C n.m.r. spectrum

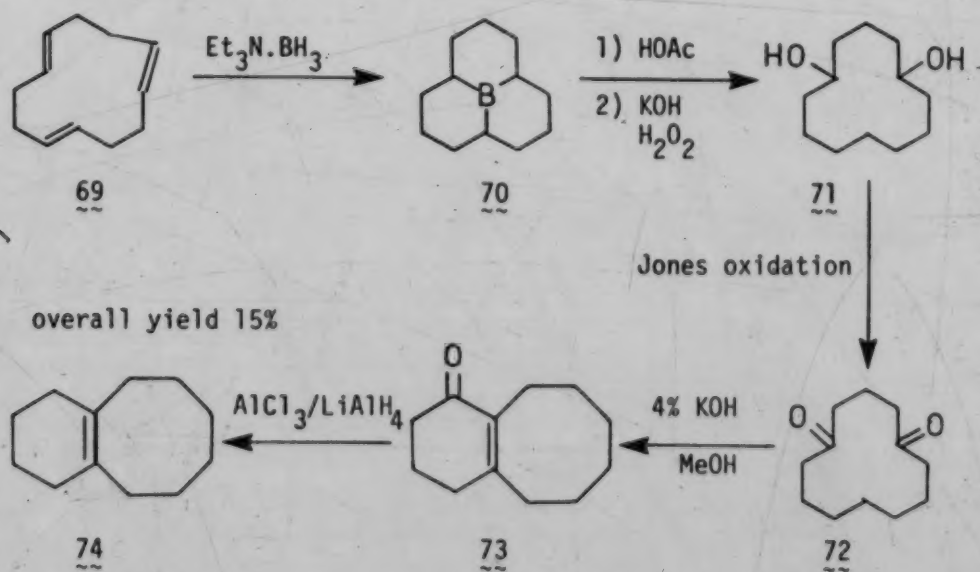
which shows only six absorptions: any other reasonable isomers of 66 would show a different number of absorptions.

The identies of all the other compounds shown in Scheme 7 were established by comparison of physical constants and specta (where possible) with the literature values.

Preparation of 1(8)-Bicyclo[6.4.0]dodecene, 74:

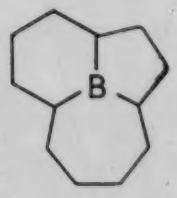
The sequence of reactions used to prepare 74 is shown in Scheme 8.

SCHEME 8

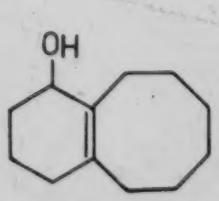


The basic sequence from 69 to 73 is due to Nozaki (123,124). In the first step Greenwood and Morris (125) suggested that the use of triethylamine borane complex not used originally by Nozaki. Also Brown (126) and Köster

(127) indicated that initially in the conversion of 69 to 70 some 75 is formed, but this can be isomerized to 70 by heating at 200°C for several hours. Even with the greatest care in the preparation of 70 only about 50% yield could be achieved as opposed to the 75% reported by Nozaki (123).



75



76

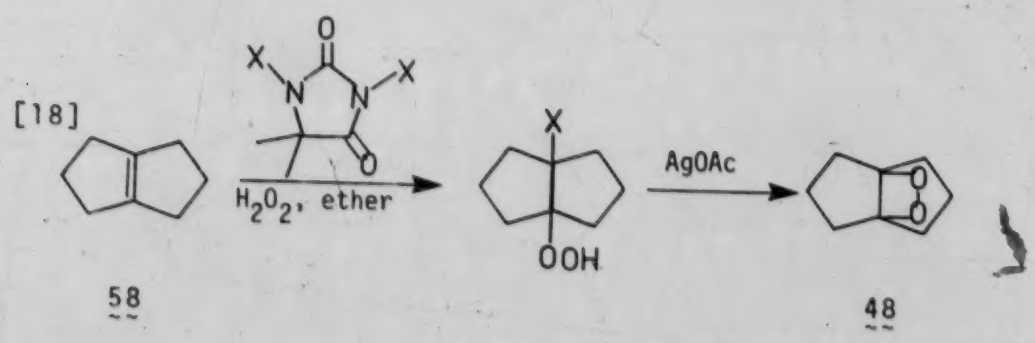
76 was prepared from 73 by reduction with lithium aluminum hydride (124). Reduction of 76 with sodium in liquid ammonia was no more successful here than in the case of 68 so reduction of 73 or 76 with aluminum trichloride/lithium aluminum hydride was used as before. 74 was purified in the same way as 66.

74 had been prepared by Niles (128) and Erman (129) who had proven its structure chemically. Here, as in the case of 66, the structure proof is based on the ^{13}C n.m.r. spectrum which again shows only six absorptions as are expected for 74 but not for any other reasonable isomers of 74.

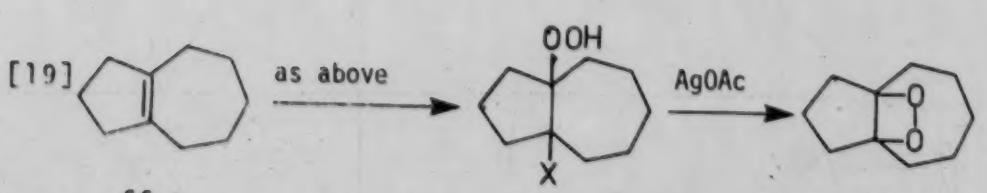
Preparation of the Dioxetanes, 48 and 49:

48 and 49 were prepared by basically the same proced-

ure as used by Filby (38) and Kopecky (5) as outlined in equations [18] and [19].



58 48



66 49

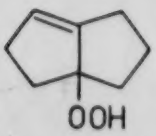
However, in these two cases it proved impossible to isolate and purify any of the β-halohydroperoxides as had been done previously (5,38). The usual techniques used to purify β-halohydroperoxides as described in Chapter I, column chromatography and crystallization, both at low temperature, failed. It soon became clear after much work, that no matter which halogen was used, isolation and characterization of a β-halohydroperoxide of either 58 or 66 was not worth the effort.

This problem was overcome by proceeding directly to the formation of the dioxetane. Treatment of solutions of crude β-halohydroperoxides with silver acetate resulted in

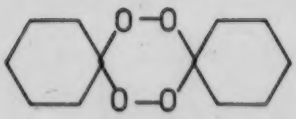
formation of the dioxetanes.

In the case of 48, reaction of AgOAc with both the β-bromo- and β-iodohydroperoxides was carried out and comparison of the results showed that the preparation using the iodohydroperoxide was more tractable. The crude product mixture could not be separated by low temperature column chromatography. However, most of the dioxetane could be removed from the reaction mixture by distillation (38). The dioxetane present in the distillate was then further purified by low temperature column chromatography. Low temperature crystallization of the dioxetane from isopentane gave a product of 92% purity in about 4% yield. Part of the loss of dioxetane resulting in this low yield was due to the distillation used in the purification. The major impurity in the crude dioxetane-containing mixture was probably the allylic hydroperoxide, 77, and this material seemed to have an affinity for the dioxetane and not all the dioxetane could be removed from it by distillation. In fact, when the bromohydroperoxide was used to prepare the dioxetane, no 48 could be distilled from the reaction mixture even though it was present. Thin layer chromatography indicated that an impurity moved with the same R_f as the dioxetane and this non-peroxidic impurity could not be separated from the dioxetane by any of the purification techniques used. This accounts for the fact that dioxetane of only 92% purity was used in the experi-

ments.



77



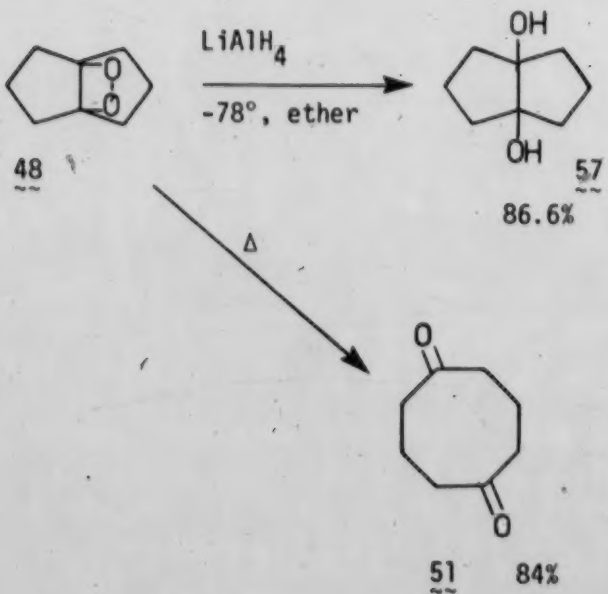
78

It is interesting to note that thin layer chromatography provides an excellent method of following any manipulations of dioxetanes. The dioxetanes appear to be quite non-polar, moving rapidly in solvents containing as little as 5% ether. While dioxetanes do not appear to react with sprays that visualize most peroxides and even the peroxide 78, they can be visualized simply by spraying the plate with a solution of 5% DBA in toluene and heating the plate in the dark. The dioxetane-containing spots then glow brightly. Thin layer chromatography of dioxetanes could be put to good use in such experiments as spotting a small amount of both 48 and 51 in the same place, heating the plate, developing it, and on visualization observing that, except for the impurity in the original dioxetane, the only product of dioxetane thermolyses was 51.

The structure of 48 was confirmed by thermolysis to a diketone and by reduction with lithium aluminum hydride to a diol. The only products obtained from these reactions (except for the small amount of original impurity) were 51 and 57 respectively, and this was confirmed in each case

by mixed melting points with authentic material. This structure confirmation is illustrated in Scheme 9.

SCHEME 9



Preparation of 49 was carried out in the same manner as for 48, that is, without isolation of the intermediate iodohydroperoxide. The iodohydroperoxide was used in this case since it appeared to give more dioxetane than the bromohydroperoxide. The crude dioxetane-containing reaction product was purified by two low temperature column chromatographies and several low temperature recrystallization from isopentane. The product, bright yellow needles, mp 57-59°C, was obtained in 26% yield with a purity of 99.5%.

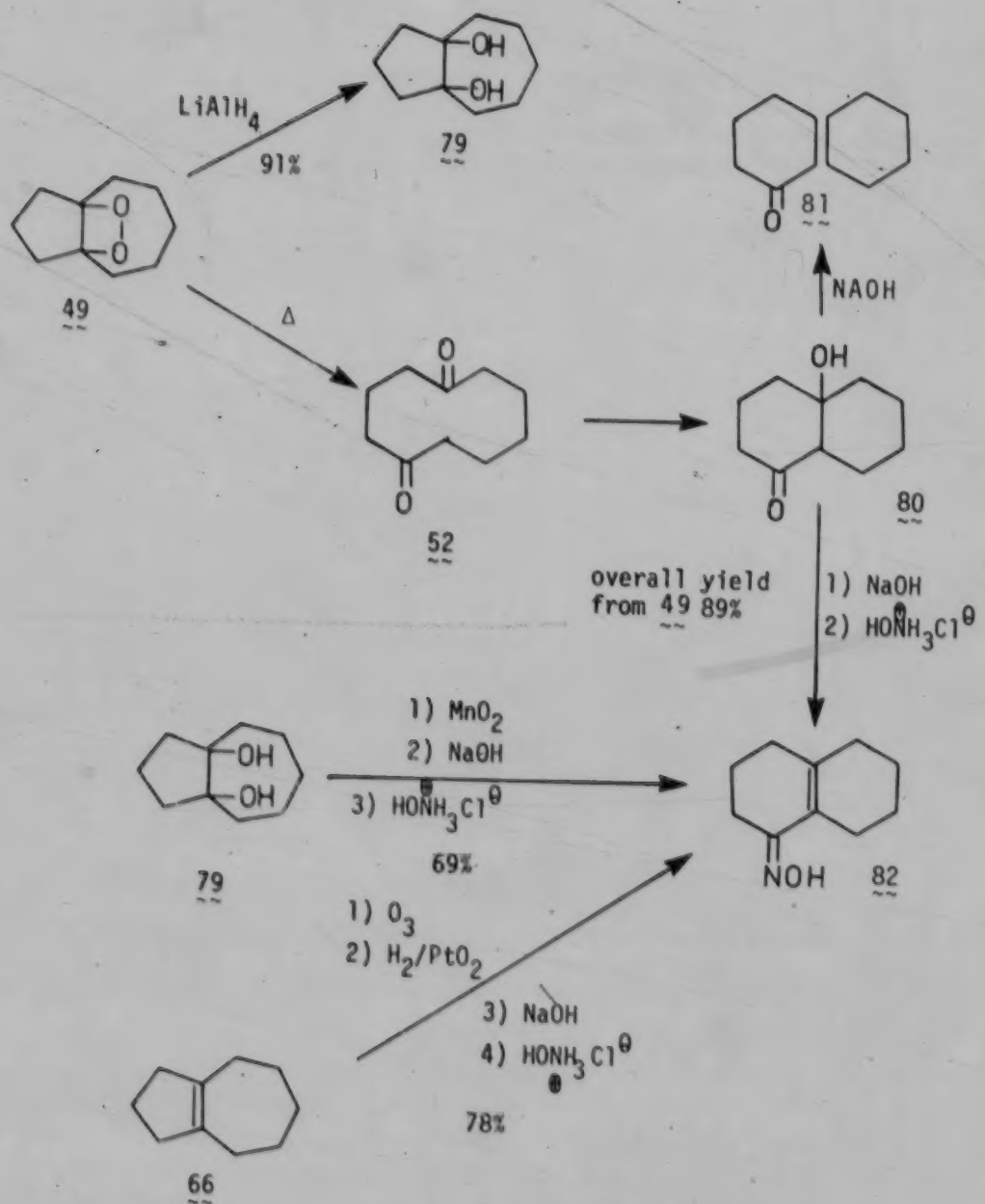
The structure of 49 was confirmed by reduction to 79 which was identified by comparison with an authentic sample prepared by osmium tetraoxide oxidation of 66. Thermolysis of 49 did not give the diketone 52. This was not unexpected since 52 should rapidly cyclize to 80 which in turn should give 81 on treatment with mild acid or base (130). A similar cyclization was observed by Filby (38). This scheme was confirmed in two ways, ozonolysis of 66 with ozone in argon (131) followed by hydrogenolysis of the ozonide to give the ketol 80 which was converted to 81 by treatment with base, and oxidation of 79 with manganese dioxide (132) to give 80 which was converted to 81 as before. 81 was identified by comparison of the melting points of its oxime and semicarbazone with the reported values (133). Then thermolysis of the dioxetane followed by treatment of the product with base and hydroxylamine hydrochloride gave 82 in good yield, confirming the dioxetane structure. These conversions are all outlined in Scheme 10.

Note that 50 could not be prepared from 74 by any variation of the methods used for the other two dioxetanes and is therefore not discussed further.

Rates of Decomposition of 48 and 49:

The decomposition of 48 and 49 were followed by observing the decay of chemiluminescence of these compounds

SCHEME 10


LiAlH4
91%
OH
OH
79
O
O
49
Δ
O
O
52
O
81
NAOH
OH
O
80
overall yield
from 49 89%
1) NaOH
2) HONH3Cl⊖
1) MnO2
2) NaOH
3) HONH3Cl⊖
69%
OH
OH
79
NOH
82
1) O3
2) H2/PtO2
3) NaOH
4) HONH3Cl⊖
78%
66

in benzene and toluene solutions respectively, using either DBA or DPA as fluorescers to enhance the luminescence to measurable intensities. It has been shown by Wilson and Schaap (50) that the presence of such fluorescers has no effect on the rate of decomposition of dioxetanes in aerated solutions. Also Filby (38) and others (50,134) have shown that the chemiluminescence decay method does measure the rate of dioxetane disappearance by comparing the results with rates obtained by iodimetry and by n.m.r. measurements. Since the observed chemiluminescence intensity (I_t) of a solution of dioxetane is proportional to the concentration of dioxetane, the rate constants for the first order decomposition of 48 and 49 were estimated graphically by plotting log I_t against time.

Several difficulties were encountered in obtaining reproducible rates for 48 and 49. 49 appeared to be very stable since temperatures over 70°C were required to obtain reasonable half lives. Part of the difficulties in getting good rates for 49 was a direct result of these high temperatures since it seemed that heat from the cell compartment was being transferred to the spectrofluorimeter electronics causing instability in the circuits of the instrument. This was avoided by keeping the hot cell out of the sample compartment until a reading was taken. While outside the instrument the sample cell was insulated and protected from light to prevent photodecomposition of

the dioxetane (50,135). Reproducible rates for 49 were only obtained when pure dioxetane was used. In the case of 48 different problems were encountered. At first, even with the purest dioxetane available, the rate plots were not first order. It was observed, however, that impure samples of dioxetane containing allylic hydroperoxide impurities gave reasonable straight lines. However this impure material could not be used for kinetics since the concentration of dioxetane could not be determined. It was found that addition of a small amount of t-butyl hydroperoxide to the pure dioxetane samples gave good straight lines and first order rate constants that were the same as those used in the end. However addition of a foreign material to straighten out the plots was hardly an acceptable solution. There was only one thing left to change, the solvent. The benzene used above was a commerical "Spectrograde" material. However, when carefully purified benzene was used for the rate determinations all the problems disappeared and t-butyl hydroperoxide was no longer necessary. Something in the original solvent must have been catalyzing the decomposition and when it reacted with either 77 or t-butyl hydroperoxide the catalytic ability was lost.

Examples of the data obtained from the decomposition of 48 and 49 are presented in Tables III and IV, respectively. First order rate plots of the data in Tables III and IV are

TABLE III

Decomposition of 9,10-Dioxa[3.3.2]propellane, 48, in Benzene at 45.1°C

Run #21

Time (s)	Meter Reading (I_t)	log I_t
420	12.70	1.104
1200	10.25	1.011
1500	9.40	0.973
1800	8.57	0.933
2400	7.08	0.850
3900	4.33	0.636
4200	3.98	0.600
4500	3.60	0.556
5100	2.98	0.474
5700	2.73	0.386
6300	1.98	0.297
7200	1.48	0.170

from graph $k = 3.19 \times 10^{-4}\ s^{-1}$

TABLE IV

Decomposition of 11,12-Dioxa[5.3.2]propellane, 49, in Toluene at 93.7°C

Run #17

Time (s)	Meter Reading (I_t)	log I_t
840	8.71	0.940
1200	7.91	0.898
1800	6.67	0.824
2400	5.63	0.751
3000	4.82	0.683
3600	4.09	0.612
4200	3.50	0.544
4800	2.98	0.474
5400	2.53	0.403
6000	2.15	0.332
6600	1.82	0.260
7200	1.55	0.190
7800	1.34	0.127

from graph $k = 2.71 \times 10^{-4}\ s^{-1}$

FIGURE 2. Rate of Decomposition of 48 in Benzene at 45.1°C.

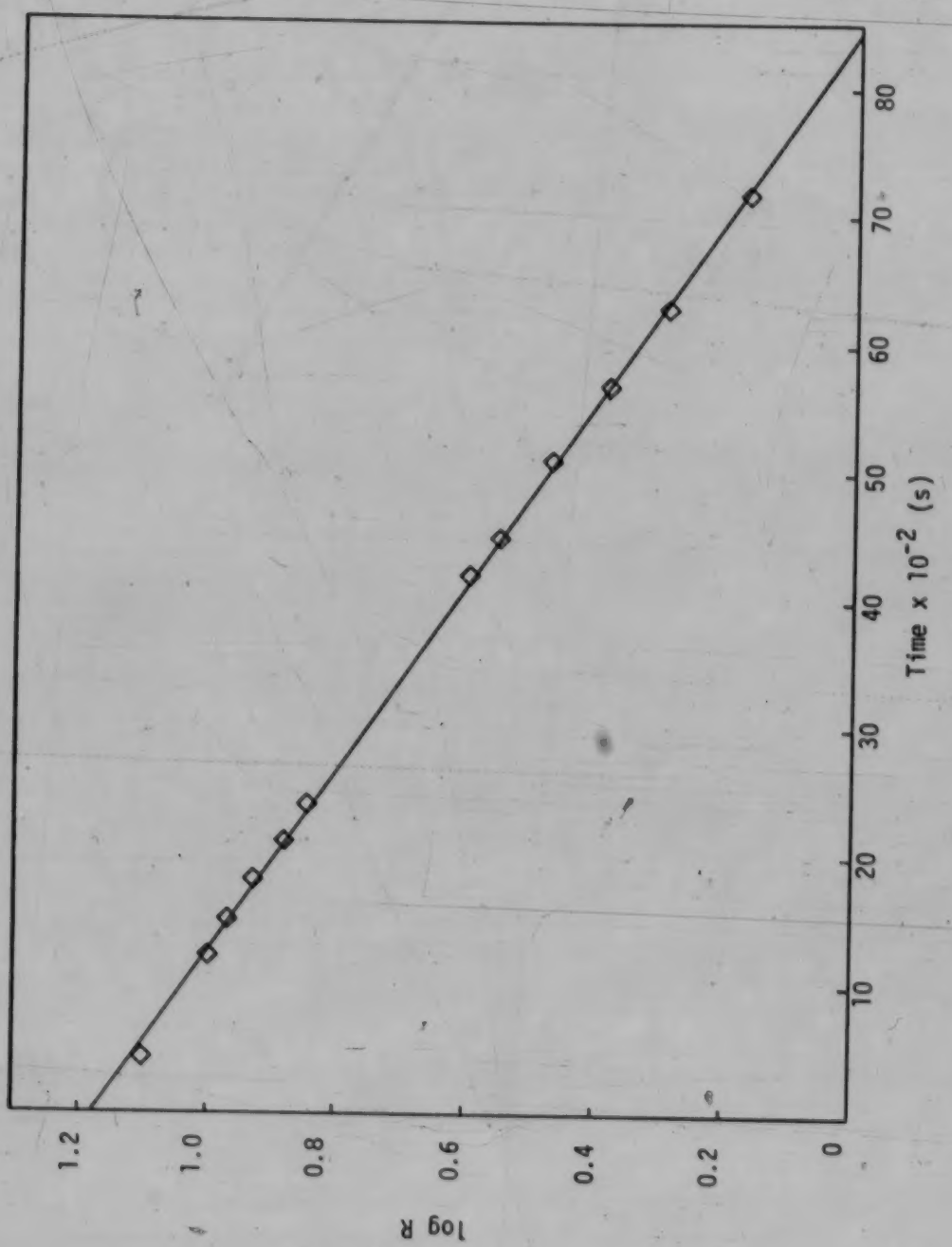
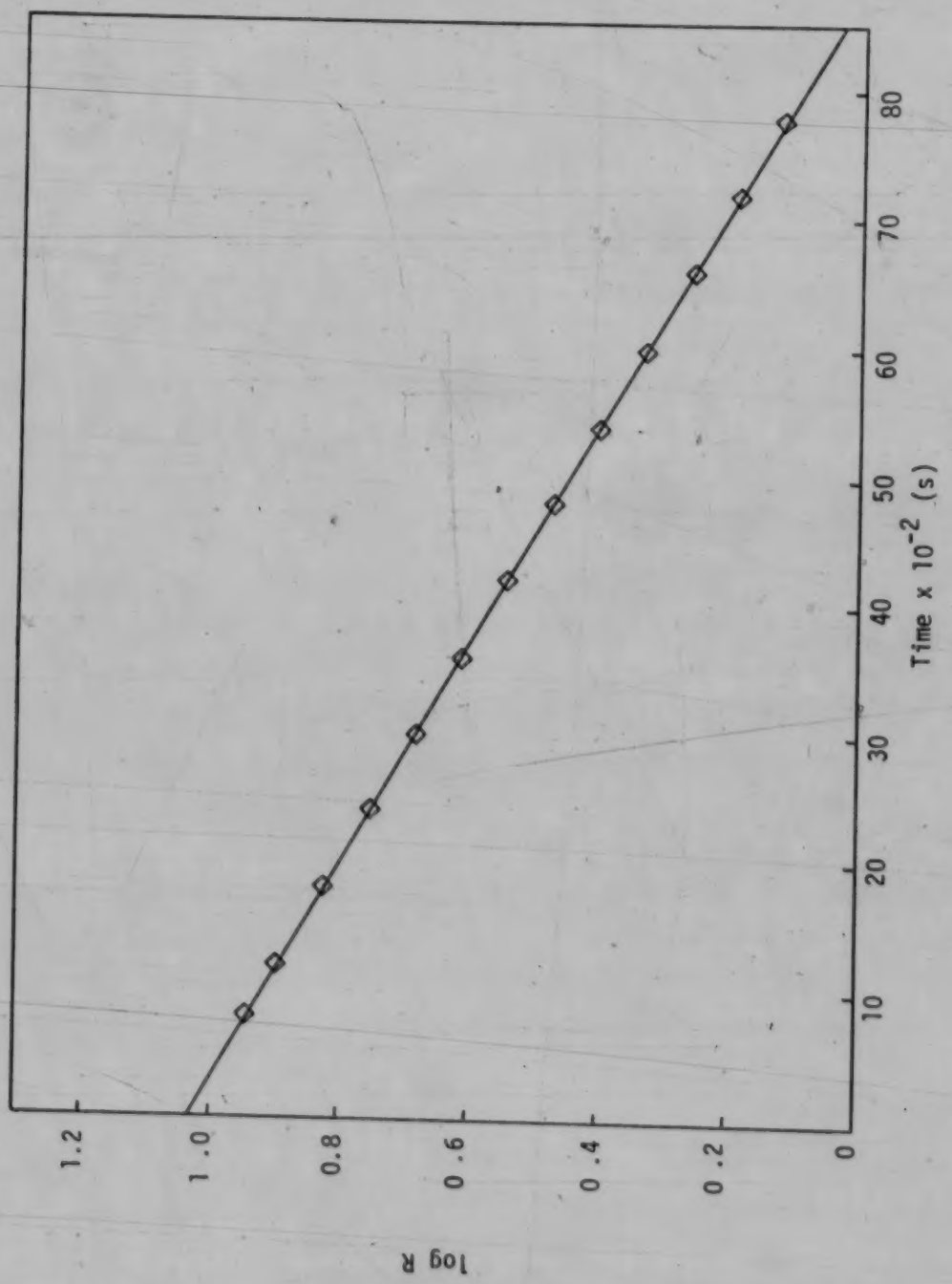


FIGURE 3. Rate of Decomposition of 49 in Toluene at 93.7°C



shown in Figures 2 and 3 respectively. Table V gives a summary of all the rate constants obtained for the thermolyses of 48 and 49.

TABLE V

Rate Constants for the Decomposition of 48 and 49

Compound	Temp (°C)	Initial Concentration (M)	Solvent	Fluorescer	Rate Constant ($s^{-1} \times 10^5$)
48	45.1	.0026	C_6H_6	DPA	33.2
48	45.1	.0022	C_6H_6	DPA	31.9
48	45.1	.0090	C_6H_6	DPA	33.3
48	45.1	.0032	C_6H_6	DPA	32.2[a]
48	45.1	.0010	C_6H_6	DBA	33.6[a]
48	25.0	.0065	C_6H_6	DPA	2.10
48	25.0	.0055	C_6H_6	DPA	2.08
48	25.0	.0090	C_6H_6	DPA	2.20
49	93.7	.0081	Toluene	DBA	27.5
49	93.7	.0081	Toluene	DBA	27.1
49	93.7	.0081	Toluene	DBA	27.3
49	75.0	.016	Toluene	DBA	3.03
49	75.0	.014	Toluene	DBA	2.97
49	75.0	.012	Toluene	DBA	3.11

[a] Run with nonpurified solvent and t-butylhydroperoxide added. This run was not used in further calculation.

Activation Energies of 48 and 49:

Using the rate data given in Table V the activation energies for the thermolysis of the dioxetanes were calculated using eq. [20] (74).

$$[20] \qquad E_A = \frac{4.576\ T_2T_1\ (\log k_2 - \log k_1)}{T_2 - T_1}$$

Enthalpies and entropies of activation were calculated from equations [21] and [22], respectively.

$$[21] \qquad \Delta H^{\ddagger} = E_A - RT$$

$$[22] \qquad \Delta S^{\ddagger} = 4.576\ (\log k_d - 10.753 - \log T + \frac{E_A}{4.576T})$$

The values of the activation parameters calculated from these equations are presented in Table VI along with Filby's (38) data for 42.

The activation energy for the thermolysis of 48 was also measured by the temperature change method described and used by Wilson (50,74). In this method two constant temperature baths at two different temperatures are connected to the spectrofluorimeter in such a way that the cell temperature can be changed rapidly. The meter reading at the first temperature is taken, the cell temperature is changed and a second meter reading is taken. Wilson (50)

TABLE VI

Activation Parameters for the Thermolysis of 1,2-Dioxetanes

Compound	E_A[a] (kcal mole^{-1})	Temperature (°C)	$\Delta H^{\ddagger}$ (kcal mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)
42	23.0 ± 0.6	29.7	22.4 ± 0.6	-1.5 ± 1
48	25.6 ± 0.6	25.0	25.0 ± 0.6	+4 ± 2
48[b]	23.3	-	-	-
49	29.8 ± 0.4	75.0	29.1 ± 0.4	+4 ± 2

[a] Errors were estimated by substituting extreme values of k_1 and k_2 into eq. [20].

[b] Determined by the temperature change method described.

has shown that as long as the concentration of dioxetane does not change very much during the equilibration time for changing to a new temperature, then the chemiluminescent intensities measured are proportional to the rates of reaction at the temperatures used. The activation energy can then be calculated from eq. [23].

$$[23] \qquad E_A = \frac{R \ln (I_1/I_2)}{\frac{1}{T_2} - \frac{1}{T_1}} - E_{\Phi_F}$$

In eq. [23], I_1 is the meter reading at T_1, I_2 is the meter reading at T_2 and E_{Φ_F} is the activation energy for fluorescence of the fluorescer used. In these experiments DPA was used as a fluorescer and for DPA $E_{\Phi_F} = 0$. The results of the temperature change experiments on 48 are shown in Table VII. Note that both temperature rise and temperature drop methods were used and both gave the same results.

Wilson (57) has shown that the temperature drop method of activation energy determination is independent of any dark reactions of the dioxetanes and that if the activation energies determined by the two methods used here differ, the temperature drop value is higher than that from rate constant determinations. Here, however, the temperature-drop activation energy is lower than the rate constant value but since the two values are within about 2 kcal mole^{-1} of each other it is probably fair to ascribe this difference

TABLE VII

Results of Temperature-Change Experiments on 48 in Benzene at 44.8°C and 24.8°C with DPA (2×10^{-2} M)

Run	Concentration of 48 (M)	I_1	I_2	E_a (kcal mole^{-1})
1	-[a]	1.12	13.4	23.4[b]
2	-[a]	1.00	11.8	23.2[c]
3	-[a]	0.94	11.2	23.3[b]
4	0.0049	1.88	22.5	23.4[b]

[a] Impure solutions of 48 were used and no concentration was determined.

[b] Temperature drop.

[c] Temperature rise.

to experimental error resulting in an average activation energy for 48 of 24.5 kcal $mole^{-1}$.

Quantum Yields of Excited State Products

The method used here to calculate the quantum yields of excited states has been used extensively by Wilson (50,74), who developed the method, and by Filby (38). It relies on the assumption that at infinite concentration of DPA all the singlet excited carbonyl products are trapped (by singlet-singlet transfer) and at infinite concentration of DBA all excited carbonyl products are trapped. The fluorescence of DPA is then a measure of the number of singlets formed. Now normally dioxetanes produce many more triplets than singlets on thermolysis (57) so that in general, excitation of DBA by singlet-singlet transfer is small compared to triplet-singlet transfer and is ignored. Thus the fluorescence of DBA is a measure of the number of triplets which transferred their energy to DBA. The efficiency of this triplet-singlet transfer for DBA is known so that the total number of triplets formed can be calculated. This method relies on the heavy atom effect in DBA which, because DBA contains two bromine atoms, causes mixing of the singlet and triplet states allowing the normally forbidden triplet-singlet energy transfer to occur (84). In order to calculate the quantum yields, the chemiluminescence intensity at infinite concentration of both DBA and DPA must be found for each dioxetane. This is done as follows.

Reactions leading to fluorescence from a solution containing dioxetane (D) and a fluorescer (F) are shown in Scheme 11. K represents a carbonyl group-containing product (50).

SCHEME 11

$$D \xrightarrow{k_1} K^* + K$$

$$F + K^* \xrightarrow{k_2} F^* + K$$

$$K^* \xrightarrow{k_3} K^*$$

$$F^* \xrightarrow{k_4} F$$

$$F^* \longrightarrow F + h\nu$$

The mechanism shown in Scheme 11 leads to the expression for the chemiluminescence quantum yield shown in eq. [24].

$$[24] \qquad \frac{1}{\Phi_{CH}} = \frac{1}{\Phi_F} + \frac{k_3}{k_2 \Phi_F} \frac{1}{[F]}$$

In eq. [24], Φ_{CH} is the chemiluminescence quantum yield and Φ_F is the fluorescence efficiency of the fluorescer, F (50). Since the chemiluminescence intensity, R, as measured by the spectrofluorimeter is proportional to the chemiluminescence quantum yield a plot of R^{-1} against $[F]^{-1}$ should be a straight line. Tables VIII and IX show the results of light emission measurements from solutions

TABLE VIII

Variation of Chemiluminescence Intensity of 48 (0.0091 M) with the Concentration of Added DPA in Benzene at 25°C

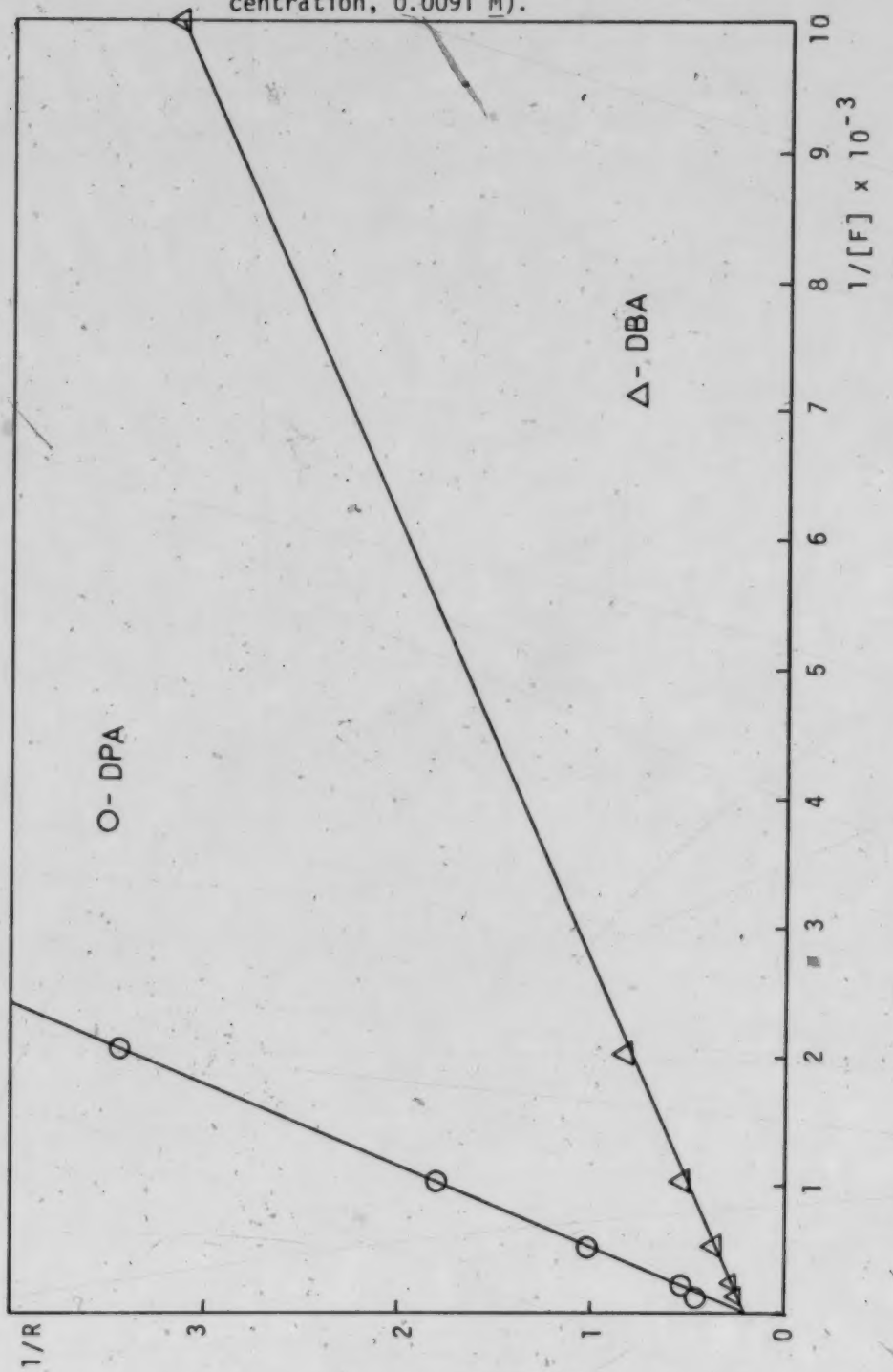
Fluorescer Concentration [F] (M)	$\frac{1}{[F]}$	Reading (R)	$\frac{1}{R}$
5×10^{-4}	2×10^{3}	.290	3.448
10^{-3}	10^{3}	.553	1.808
2×10^{-3}	5×10^{2}	.992	1.008
5×10^{-3}	200	1.92	0.521
8×10^{-3}	125	2.465	0.406
10^{-2}	100	2.90	0.345

TABLE IX

Variation of Chemiluminescence Intensity of 48 (0.0091 M) with the Concentration of Added DBA in Benzene at 25°C

Fluorescer Concentration [F] (M)	$\frac{1}{[F]}$	Reading (R)	$\frac{1}{R}$
10^{-4}	10^{4}	.318	3.145
5×10^{-4}	2×10^{3}	1.20	0.833
10^{-3}	10^{3}	1.915	0.522
2×10^{-3}	500	2.74	0.365
5×10^{-3}	200	3.65	0.274
8×10^{-3}	125	3.86	0.259
10^{-2}	100	3.98	0.251

FIGURE 4. Effect of Fluorescer Concentration [F] on the Relative Intensity of Chemiluminescence from 48. (Dioxetane Concentration, 0.0091 M).



of 48 in the presence of DPA and DBA. Figure 4 shows plots of the data in Tables VIII and IX.

The measurements were taken at temperatures such that the concentration of dioxetane did not change while the reading was being taken. Plots of R^{-1} against $[F]^{-1}$ for DBA were all linear in the range 10^{-4} to 10^{-2} M of fluorescer indicating that the fluorescence of DBA occurs via excitation by a single species of excited state (50). Plots for DPA are linear in the range 10^{-2} to 5×10^{-4} M in fluorescer, but the difference in slope shows that DPA is being excited by a different species of excited state than DBA. Wilson (50) has shown that DBA is excited by triplet-singlet energy transfer from the triplet carbonyl products of dioxetane decomposition while DPA is excited by the singlet carbonyl products, and this forms the basis for the determination of quantum yields as described in the next section. Readings for DPA or DBA at concentrations higher than 10^{-2} M were not taken since self-quenching of fluorescence produces incorrect readings (38).

Table X shows the results for light emission measurements for 40 and 49 as well as 48. Values for 40 were determined since this compound was to be used as a light standard as suggested by Filby (38).

Before the quantum yields can be determined the specrofluorimeter must be calibrated. The light standards available for convenient use are the radioactive standard

TABLE X

Slopes and Intercepts of the Double Reciprocal Plots of Chemiluminescence Intensity and Fluorescer Concentration in Benzene

Dioxetane	Concentration (M) x 10^2	Fluorescer	Temp (°C)	Slope of 1/R vs 1/[F] x10^{-3}	$1/R_\infty$ [a]	R_∞
40	1.02	DPA	45.0	4.18	7.43	0.135
40	1.02	DBA	45.0	1.41	0.197	5.086
48	0.91	DPA	25.0	1.61	0.199	5.025
48	0.91	DBA	25.0	0.30	0.221	4.527
49	0.74	DPA	69.0	7.89	2.02	0.495
49	0.74	DBA	69.0	1.25	0.81	1.235

[a] R_∞ is the spectrofluorimeter reading at infinite concentration of fluorescer obtained by extrapolation.

of Hastings (136) and the luminol standard of Lee and Seliger (137). Both of these have major drawbacks to their application. The Hastings standard gives off only weak emission and thus can only be used to calibrate sensitive instruments. The luminol standard is easy to prepare and gives off a bright light but it is difficult to use in practice. Filby suggested that 40 would provide a very convenient light standard. 40 is easy to prepare pure, gives off a reasonable intensity of light on thermolysis and because it is the most studied of all dioxetanes (79,82,83,93,140,141) its excited state yields are well known. The excited state yields of 40 used to calibrate the spectrofluorimeter here are based on the luminol standard and are due to Kopecky (39). These yields are 2.5×10^{-4} for singlet acetone and 0.221 for triplet acetone. These values are in excellent agreement with recent values of Adam (91). Other authors have used 40 as a standard as well (97,140).

The excited state quantum yields can then be calculated as follows. The absolute chemiluminescence intensity I is given in eq. [25] where R_∞ is the spectrofluorimeter reading at infinite concentration of fluorescer and K_F is the instrument calibration constant for solutions containing fluorescer F.

[25] $$I = R_\infty \times K_F$$

The chemiluminescence quantum yield is then given by eq. [26] where k_d is the rate constant for the decomposition of the dioxetane at the temperature in question, [D] is the concentration of dioxetane in one milliliter of solution and A_o is Avogadro's number.

[26] $$\Phi_{CH} = \frac{I}{k_d[D]A_o}$$

The chemiluminescence is related to the yield of excited states $\Phi_{D \rightarrow K^*}$ by eq. [27] where Φ_{Et} is the quantum yield of energy transfer from the excited product to the fluorescer, F, and Φ_F is the quantum yield for fluorescence of F.

[27] $$\Phi_{CH} = \Phi_{D \rightarrow K^*} \Phi_{Et} \Phi_F$$

Before equations [25] - [27] can be applied several other factors must be considered. The observed chemiluminescence intensity can be affected by several factors, quenching of fluorescence by dioxetane and quenching by dissolved oxygen. It has been shown that 1,2-dioxetanes quench the fluorescence of DPA (50) and biacetyl (147) but at the low concentrations of dioxetane used here this quenching effect should be small and is ignored here (50). However quenching of fluorescence by dissolved oxygen has been shown to be about 20% in the case of DPA (50). Thus

this value of 20% quenching is probably reasonable at 45°C or less but at 69°, considerable outgassing of the solvent was observed. Less dissolved oxygen in the solution may result in less quenching of DPA at higher temperatures and so values of singlet quantum yields at 69° should be considered as maximum values. With this proviso in mind all instrument readings involving DPA are increased by 20% and are denoted by R_{∞}^{corr}. For DBA, rapid intersystem crossing to the triplet state (83) results in a shortened singlet lifetime that is too short to be efficiently quenched by oxygen. Normally dioxetanes produce many more triplets than singlets on thermolysis (57) and so excitation of DBA by singlet-singlet transfer is generally small and ignored. However, when the yield of singlet excited state product is close to the yield of triplet products a correction for singlet DBA produced from singlet products must be used. With these corrections in mind we can proceed.

The only values in equations [25] to [27] not determined here are Φ_{Et} and Φ_F. For DPA, Φ_F is unity and temperature independent (83) and at infinite concentration of DPA all ketone singlets should be trapped by an allowed singlet-singlet transfer to DPA so that Φ_{Et} is also unity. For DPA, eq. [27] becomes eq. [28]

[28] $$\Phi_{CH} = {}^1\Phi$$

For DBA however, Φ_{Et} is about 0.2 (142) and Φ_F is 0.1 at 20°C but it is also temperature dependent. The exact temperature dependence of Φ_F is not known but Wilson assumes that it is similar to that of 9,10-dichloroanthracene with an activation energy for fluorescence of -4.5 kcal mole^{-1}. Thus, using the methods of Wilson (74) Φ_F for DBA was calculated to be 0.093 at 25°C and 0.036 at 69°C. In order to calculate $^3\Phi$ from eq. [27] these values must be used.

The calibration constants may now be calculated. For DPA, Kopecky (39) reported that for 40 at 45.0°C, $k_D = 1.34 \times 10^{-5}$ s^{-1} and $^1\Phi = 2.5 \times 10^{-4}$. From Table X, for solutions of 40 containing DPA we find $R_\infty = 0.135$ and [D] = 0.0102 M. Correcting for oxygen quenching of DPA R_∞ becomes $R_\infty^{corr} = 0.169$. Substituting in equations [28], [26] and [25] we find $K_{DPA} = 1.219 \times 10^{11}$ photons ml^{-1} s^{-1} per spectrofluorimeter unit. Similarly for DBA using Kopecky's (39) value of $^3\Phi$ of 0.221 at 45° Φ_{DBA} = 0.065 (38) and data from Table X for 40 and DBA we find $K_{DBA} = 4.65 \times 10^{10}$ photons ml^{-1} s^{-1} per spectrofluorimeter unit.

By using these two calibration constants, the data in Table X and equations [25] to [28] the excited state yields, $^1\Phi$ and $^3\Phi$ for 48 and 49 can be obtained. All pertinent data and the results are shown in Table XI.

TABLE XI

Yields of Excited State Carbonyl Products from Thermolysis of 1,2 Dioxetanes in Benzene Solution

Compound	Concentration (M) x 10^2	Fluorescer	R_∞	R_∞^{corr}	Temp. (°C)	k (s^{-1}) x 10^5	$^*\Phi_{CH}$[b] x10^3	$^1\Phi$ x10^3	$^3\Phi$	$^3\Phi/^1\Phi$
40	1.02	DPA	0.135	0.169[c]	45.0	1.34	0.25	0.25	-	880
40	1.02	DBA[f]	5.086	5.086	45.0	1.34	2.87	-	0.22	
48	0.91	DPA	5.025	6.281[c]	25.0	2.13	6.60	6.60	-	13
48	0.91	DBA[e]	4.527	3.923[d]	25.0	2.13	1.80	-	0.084	
49	0.74	DPA	0.495	0.619[c]	69.0	1.43	1.18	1.20	-	104
49	0.74	DBA[g]	1.235	1.235	69.0	1.43	0.90	-	.125	

[a] Rate constant for the decomposition of the dioxetane at the temperature indicated.

[b] Chemiluminescence quantum yield.

[c] Corrected for quenching of singlet DPA by oxygen.

[d] Corrected for the fraction of DBA excited by transfer from singlet products.

[e] Φ_{DBA} at 25° = 0.093

[f] Φ_{DBA} at 45° = .065

[g] Φ_{DBA} at 69° = .036

DISCUSSION

As indicated in the introduction this research was undertaken in an attempt to explain the results of Filby (38) who had shown that the singlet and triplet yields from 42 were abnormally low when compared with other dioxetanes. Filby had pointed out that if strain was present in the product ketone then there might not be enough energy available to efficiently excite the product. This is best illustrated by the following example calculation of the energy available from thermolysis of 42, as shown below.

42 64

The energy available from the decomposition of a dioxetane, $\mathcal{E}_D$, is given by eq. [29].

[29] $$\mathcal{E}_D = \Delta H_f^o(\text{products}) - \Delta H_f^o(\text{dioxetane}) - E_A$$

The heats of formation of the dioxetane and the dione can be calculated by using Benson's additivity method (93,94). Using 42 as an example:

[30] $$\Delta H_f^o\ (42) = 8[C\text{-}(H)_2(C)_2] + 2[C\text{-}(C)_3(O)] + 2[O\text{-}(O)(C)] + \text{corrections.}$$

[31] ΔH_f^o (42) = 8(-4.95) + 2(-4.5) + 2(-6.6) + corrections

The corrections involved here include the following, which must be added to eq. [31]; the dioxetane ring strain of 25 kcal mole^{-1} as used by Richardson (39), four ether-oxygen gauche interactions at 0.5 kcal mole^{-1} each, and a correction for the cis-decalin system in 42, 1.6 kcal mole^{-1}. Eq. [31] becomes

[32] ΔH_f^o (42) = 8(-4.95) + 2(-4.5) + 2(-6.6)
+ 25 + 2 + 1.6 = -33.2 kcal mole^{-1}

For the dione, 64, the calculation is given by eq. [33]

[33] ΔH_f^o (64) = 4[C-(H)$_2$(C)$_2$] + 4[C-(H)$_2$(C)(CO)]
+ 2[(CO) - (C)$_2$] + corrections

Here the only correction is the strain in the 1,6-cyclodecandione ring. Filby (38) estimated this value to be somewhere between 0 and 13 kcal mole^{-1}. Eq. [33] becomes

[34] ΔH_f^o (64) = 4(-4.95) + 4(-5.2) + 2(-31.4) + Strain (64)
= Strain (64) - 103.4 kcal mole^{-1}

Substituting all values known into eq. [29] and using Filby's value of E_A as +22.9 kcal/mole (38)

[35] $\underset{\sim}{\mathcal{E}}_{\underset{\sim}{42}} = -103.4 + 33.2 - 22.9 + \text{Strain } (\underset{\sim}{64})$

$= -93.1 + \text{Strain } (\underset{\sim}{64})$

From eq. [35] it is easy to see how important the strain in the dione ring is. If strain ($\underset{\sim}{64}$) = 0 then $\underset{\sim}{\mathcal{E}}_{\underset{\sim}{42}} = -93.1$ and if strain ($\underset{\sim}{64}$) = 13 then $\underset{\sim}{\mathcal{E}}_{\underset{\sim}{42}} = -80.1$ kcal mole^{-1}. Assuming that carbonyl compounds in general have about the same requirements for excitation as acetone (singlet, 85 kcal mole^{-1} and triplet, 78 kcal mole^{-1} (96)), then the strain in the dione ring dictates whether enough energy is available to form singlet products.

Since Filby's work two reports of the strain in the 1,6-cyclodecanedione ring have appeared. Benson (94) reported that the strain in cyclodecanone was 3.6 kcal mole^{-1} based on the difference between the actual experimental value of the heat of formation due to Wolf (143) and the value calculated by Benson's additivity rules. The strain in 1,6-cyclodecanedione must be less than 3.6 kcal mole^{-1} since introduction of a second sp^2 centre should reduce the strain in the ten-membered ring even further (144,147). Thus,on Benson's scale the ring strain correction for $\underset{\sim}{64}$ is probably $0 \leq \text{Strain } (\underset{\sim}{64}) \leq 3$ kcal mole^{-1}. However Allinger (144) has reported a value of 8.22 kcal mole^{-1} for the strain in $\underset{\sim}{64}$. Study of Allinger's results (144) shows that his method of calculation gives a value for the

heat of formation of cyclodecanone of -67.18 kcal mole^{-1} while Wolf reports (143) that the experimental value is -72.91 kcal mole^{-1} a difference of almost 5 kcal mole. Since Allinger's method does not give a reasonable value for the heat of formation of cyclodecanone (or cyclooctanone for that matter, Allinger ΔH_f^o = -59.32, experimental (143) -65.05) Benson's values, which are based on experimental results are used in the rest of the discussion. Thus, using Benson's values for the strain energy we find $-90.1 \leq \mathcal{E}_{\underset{\sim}{42}} \leq -93.1$ kcal mole^{-1} from eq. [35].

If the calculation done on 42 is repeated for 48 and 49 the following results are obtained. The energy available from 48 is $\mathcal{E}_{48} = -103.2$ (based on Benson's value of 1.5 for the strain in cyclooctanone, the strain in 1,5-cyclooctanedione was set equal to zero). The energy available from 49 is $-107.1 \leq \mathcal{E}_{49} \leq -110.1$ kcal mole^{-1} using the same ring strain correction for 52 (0 - .3 kcal mole^{-1}). Table XII is a summary of the energies available from decompositions of several dioxetanes and it can be seen that in each case shown there appears to be enough energy to excite the product ketone to either its singlet or triplet state.

The reason for the difference between the available energy of 40 and 42, and 48 and 49 is that 48 and 49 have strain energy inherent in their fused ring systems (per 5-membered ring, 6.3 and per 7-membered ring, 6.4 kcal mole^{-1})

TABLE XII

Energy Available from Thermolysis of 1,2-Dioxetanes

Dioxetane	ϵ_D (kcal mole^{-1})
40	-92.1
42	-90.1 to -93.1
48	-103.2
49	-107.1 to -110.1

that is not present in 40 and 42.

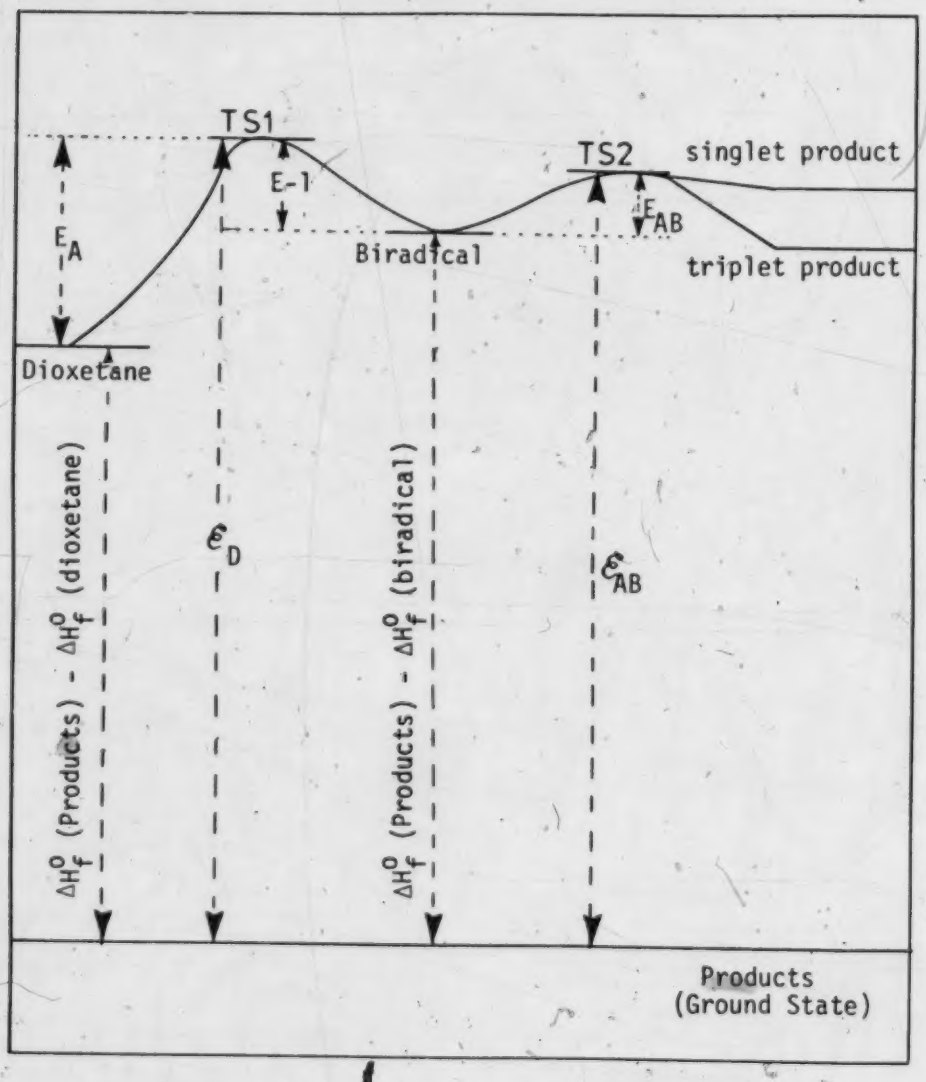
However, Wilson (57) has pointed out that available energies as calculated above by Richardson's method (89) should probably be considered as the maximum possible values if Richardson's biradical mechanism is correct. Figure 5 shows a schematic diagram of the energetics of dioxetane decomposition based on the biradical mechanism. If the picture in Figure 5 is correct then eq. [29] should actually be eq. [36].

[36] $$\mathcal{E}_{AB} = \Delta H_f^o(\text{product}) - \Delta H_f^o(\text{biradical}) - E_{AB}$$

Wilson thus suggests that, in fact, $\mathcal{E}_{AB}$ is the energy available on dioxetane thermolysis not $\mathcal{E}_D$. It is possible to imagine that based on Figure 5, even if $\mathcal{E}_D$ is large enough to excite the products to both possible states, $\mathcal{E}_{AB}$ may not be large enough since $\mathcal{E}_{AB}$ depends on the value of E_{AB} which is unknown. Of course the whole argument rests on the exact energies of the triplet and singlet states of the product.

Unluckily in this work it was not possible to determine if the lack of availability of excitation energy was the cause of the low yields of triplet excited states 48 and 42. However, even though calculations show that enough energy is available, Wilson's arguments show that lack of excitation energy may still be the explanation for the low excited state yields.

FIGURE 5. Schematic Diagram of the Energetics of Dioxetane Decomposition based on the Biradical Mechanism of Richardson (59, 89).



As eq. [29] indicates, the energy available from dioxetane thermolysis is assumed to be the sum of the differences in enthalpies of formation of reactants and products minus the activation energy. Perrin (98) however, suggested that the available energy should be related to the change in free energy in going from reactants to products. In other words, entropy as well as enthalpy but not activation energy must be considered. Perrin uses 40 as an example and shows that enough energy is available to excite acetone. However in the case of 40 decomposing to two separate acetone molecules the change in entropy is large, but in the case of the tricyclic dioxetanes the change in entropy will be much smaller since only one molecule is formed on thermolysis. Perrin's scheme would predict that excitation of the cyclic diones formed on thermolysis of tricyclic dioxetanes would not be possible. The data presented in this chapter show that both singlet and triplet excited cyclic diones are formed. Perrin also stated that based on an isothermal thermodynamic cycle, thermodynmaics should limit the quantum yield of a chemiluminescent reaction. Perrin's theoretical arguments have been shown to be incorrect by both Lissi (99) and Wilson (100), in agreement with the experimental evidence.

As well as calculating the energy released on dioxetane decomposition, Benson's methods (93-95) can also be

used to estimate the activation energy of the decomposition based on the biradical mechanism (78,79). This method is based on Figure 4 and outlined in eq. [37]. The heat

[37] $E_A = \Delta H_f^o(\text{biradical}) - \Delta H_f^o(\text{dioxetane}) + E_{-1}$

of formation of the biradical, ΔH_f^o(biradical), can be calculated as shown below, using Benson's additivity values for radicals (95). For 42, ΔH_f^o (42) is -33.2 kcal mole^{-1} from eq. [33] and E_{-1} = 8.5 kcal mole^{-1} (89). ΔH_f^o(biradical) can be calculated as follows.

[38] $\Delta H_f^o(\text{biradical}) = 8[C(H)_2(C)_2] + 2[\dot{C}(O)(C)_3]$ + corrections

$= -22.4$ + corrections kcal mole^{-1}

The corrections include 1.6 kcal mole^{-1} for the cis-decalin system, 2.0 kcal mole^{-1} for the four ether-oxygen gauche interactions, and 0.5 kcal mole^{-1} for the interaction between the two oxygen atoms. Eq. [38] becomes

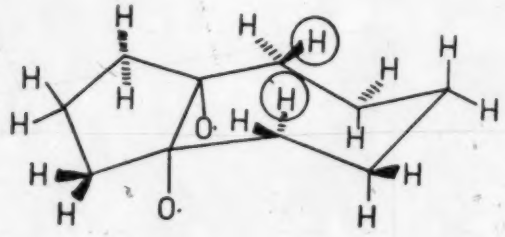
[39] $\Delta H_f^o(\text{biradical}) = -22.4 + 1.6 + 2.0 + 0.5 = -18.3$ kcal mole^{-1}

Substituting in eq. [37] the activation energy is

[40] E_A (42) = -18.3 + 33.2 + 8.5 = 23.4 kcal/mole.

Similar calculations show that the activation energies for all tricyclic dioxetanes should fall in the range 22 - 24 kcal mole^{-1}. Table VI shows that while 42 and 48 fall in or near this range 49 with an activation energy of almost 30 kcal mole^{-1} does not fit the mold. The reasons for this

are most probably steric. Molecular models of 49 show that if it opens to the biradical the two dioxetane oxygen atoms move apart forcing some of the ring hydrogens together. This is illustrated below for one conformation of the biradical. The hydrogens circled are closer together in the biradical than in the dioxetane. Other conformations of the biradical suffer from the same sort of unfavourable interactions.

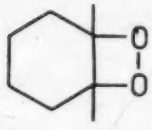
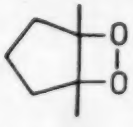
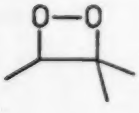


These transannular interactions occurring on biradical formation require energy to overcome, resulting in a higher activation energy and a slower rate of decomposition. These sorts of unfavourable interactions can be avoided in both 48 and 42 and so the activation energies for these compounds are much closer to the calculated values.

Table XIII gives a list of excited state yields of some dioxetanes. One of the problems encountered when comparing yields of excited states is that different authors use different light standards and unluckily the different standards in use do not give mutually consistent results. Three light standards in general use are the radioactive standard of Hastings (136) used by Wilson,

TABLE XIII

Excited State Yields from Several Dioxetanes

Dioxetane	$^1\Phi \times 10^3$	$^3\Phi$	$^3\Phi/^1\Phi$	Source
40	0.25	0.22	880	(39)
40	0.35	-		(91)
42	0.0026	0.0081	3115	(38)
	0.2	0.17	850	(38)
41	<0.05	0.1	2000	(50)
47	5.0	0.05	10	(74)
48	6.6	0.084	13	
49	1.2	0.125	104	
	1.5	0.10	67	(140)
	0.4	0.125	313	(82)
	1.0	0.25	250	(140)

another radioactive standard used by Adam (56,91) and the luminol standard of Lee (137) used by Kopecky and also indirectly in this work. Approximate conversion factors to the luminol standard are about 0.5 for the Hastings' standard and 0.67 for Adam's standard. The values in Table XIII have been converted to the luminol standard using the conversions above.

Of the tricyclic dioxetanes known, only 49 has excited state yields similar to those of the open chain dioxetanes. It also appears impossible to explain the variation in the excited state yields of the three tricyclic dioxetanes on structural grounds. Wilson (74) cannot explain the low yield of triplet obtained on thermolysis of 47 either. More work is necessary before the factors affecting the absolute and relative yields of singlet and triplet excited carbonyl compounds from thermolysis of dioxetanes can be determined. Probably several factors are at work because, while 42 has a reduced overall excited state yield and a very high triplet to singlet ratio, 48 has a reduced overall yield but a low triplet to singlet ratio. The similarities in the yields of excited states between 48 and 47 are difficult to understand on the basis of dioxetane structure since the structures of the compounds are so radically different. Comparison of Tables XI and XII does show that having large amounts of energy available for excitation does not result

in a dioxetane giving more excited product than obtained from a dioxetane with less available energy. For example, 49 has considerably more available energy than 40 but the yields of excited products are not very different.

This work has provided more examples of dioxetanes which behave diffently from the norm. The fact that the three tricyclic dioxetanes known all behave differently with respect to triplet/singlet energy partitioning must be consistent with any mechanism purporting to explain the production of excited state products from dioxetane thermolysis. Also, it has been shown that a tricyclic structure in a dioxetane does not prevent excited state production similar to the excited state production in simpler dioxetanes such as 40.

EXPERIMENTAL

The instruments used in this section were the same as those used in Chapter I. ^{13}C n.m.r. spectroscopy was done on either a Varian HA100-15 or a Brücker HFX-10 spectrometer. The exact mass measurements in mass spectroscopy were done on an AEI MS-50 spectrometer. The spectrofluorimeter used was a Turner Model 430.

Hydrocarbon solvents were purified as outlined in Chapter I. Anhydrous tetrahydrofuran was prepared by refluxing the solvent over calcium hydride for 2 h and then distilling from calcium hydride onto freshly activated molecular sieves, type 4A. Acetone was purified by refluxing over potassium permanganate for 1 h and then distilling onto freshly activated molecular sieves, type 4A. Benzene and toluene were purified by washing with concentrated sulphuric acid until the acid layer remained colourless, washing with water, drying over $MgSO_4$ and distilling twice rejecting one tenth of the total volume as preflow and another tenth as residue. Triethyl orthoformate was purified by distillation. DPA was purified by recrystallization from toluene.

Dry, inert atmospheres of either nitrogen or argon were supplied by passing the gas through Feiser's solution, 10% lead acetate solution, sulphuric acid, sodium hydroxide and anhydrous calcium sulphate.

Drying of solutions was done with magnesium sulphate/calcium sulphate for ether solutions and with magnesium sulphate for other solvents, unless otherwise noted.

Removal of solvents from solutions was done on a rotary evaporator equipped with a dry-ice condenser and a bath at room temperature unless otherwise noted.

1,5-Cyclooctanediol, 56: (105,107,108)

To a two liter, three-necked flask equipped with a reflux condenser, a pressure-equalized dropping funnel, a magnetic stirrer and a nitrogen inlet and outlet was added 1 M borane in tetrahydrofuran solution (800 ml, 0.8 moles). The transfer was made under a flow of dry nitrogen using a syringe equipped with a syringe valve. The flask was purged with dry nitrogen before addition and it was kept under a constant pressure of dry oxygen-free nitrogen during the following procedure. To the borane solution 1,5-cyclooctadiene (86.4 g, 0.8 moles) made up to 200 ml with anhydrous tetrahydrofuran, was added dropwise over 30 m. The clear reaction mixture was refluxed one hour and cooled to 0°C in an ice-salt bath. A precipitate formed. 6N sodium hydroxide solution (400 ml) was added very carefully while maintaining the reaction temperature below 10°C with the ice-salt bath. 30% hydrogen peroxide (300 ml) was added dropwise while maintaining the reaction temperature below 10°C. The reaction mixture

consisted of two layers, so the aqueous layer was saturated with potassium carbonate and the organic layer was separated, dried and evaporated to an oil. This oil was co-evaporated once with 98% ethanol and twice with carbon tetrachloride, to give a white, crystalline mass. Thin layer chromatography (ether) indicated that the product was virtually pure, yield 115 g (100%). A small portion of this material was purified by column chromatography on silica gel (eluant ether) to give a white crystalline solid, m.p. 72 - 74°C, reported (105,107) 73.5 - 74.5°C.

The i.r. spectrum (nujol) showed absorptions at 3260 cm^{-1} (O-H stretch).

The n.m.r. spectrum (DMSO-d_6) showed absorptions at τ 5.78 (d, OH) and τ8.5 (broad).

1,5-Cyclooctanedione, 51: (109,110,146)

Crude 56 (72 g, 0.5 moles) prepared above was dissolved in purified acetone (1000 ml) and Jones reagent (146) was added dropwise while keeping the reaction temperature below 30°C. Addition of the oxidant was continued until a pronounced yellow-orange colour persisted in the solution for more than 10 m. The acetone was then decanted from the green precipitate and the precipitate was washed well with fresh acetone. The combined acetone solutions were stirred with 2-propanol (10 ml) to destroy excess reagent and then sodium bicarbonate (5 g) was added. The solution

was filtered through "Celite" and the acetone was removed. Water (200 ml) was added to the residue and the resulting solution was extracted with dichloromethane (4 x 100 ml). The combined organic extracts were washed with water (50 ml) and dried. Removal of the solvent gave oily white crystals. This material was dissolved in purified acetone (1000 ml) and the oxidation step was repeated until the second endpoint was reached. This took about 10 h. The reaction mixture was worked up as before to yield 42 g of a yellowish oily solid. This was recrystallized from ether/pentane (2x) to give pure white needles, 23 g (33%), m.p. 71 - 72°C as reported (109).

The i.r. spectrum ($CHCl_3$) showed absorption at 1710 cm^{-1} (C=O stretch), reported (109) 1698 cm^{-1}.

The n.m.r. spectrum ($CDCl_3$) showed absorption at τ 7.6 (broad).

1,5-Bicyclo[3.3.0]octanediol, 57: (101,111)

Zinc amalgam was prepared by shaking mossy zinc (110 g) for 3 m with a solution of mercuric chloride (11 g) in water (125 ml) and concentrated hydrochloric acid (3 ml). The liquid was poured away and the amalgamated metal was washed well with water. The amalgam was added to 6 M hydrochloric acid (140 ml) and 51 (6 g, 0.043 moles) was added. This reaction mixture was shaken for 30 m and then the solution was decanted from the metal. The

remaining metal was washed well with water and the combined aqueous solutions were saturated with sodium chloride and continuously extracted for 14 h with dichloromethane. The dichloromethane extracts were neutralized with sodium bicarbonate (4 g) and dried. Concentration of the organic layer gave a white solid that was recrystallized from carbon tetrachloride to yield a crystalline solid, 5 g (93%), m.p. 64.5 - 65.5°C, reported (101), 61.5 - 62°C.

The i.r. spectrum ($CHCl_3$) showed absorption at 3460 cm^{-1} (O-H stretch).

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 6.90 (s, OH) and τ 8.3 (broad) in a ratio of 1:6.2, required 1:6.

3-Ethoxy-2,4-dioxatricyclo[3.3.3.0]undecane, 60: (112-114)

57 (10 g, 0.07 moles) and purified triethyl orthoformate (10.3 g, 0.07 moles) were mixed in a flask connected to a short path distillation apparatus. The distillation flask was heated to 130° and after about 10 m, ethanol began to distill. After one-half hour no more ethanol could be collected so a small chip of sodium metal was added to the pot and the residue was distilled to give a clear oil, b.p. 74 - 76°C (2.7 torr), yield 12.0 g (85%) and n_D^{20} 1.4590.

The i.r. spectrum (neat) showed absorption at 2960 cm^{-1} (C-H stretch).

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 4.30 (s, methine proton), τ 6.51 (q, J = 7 Hz, ethoxy group), τ 8.25 (broad, ring methylene protons) and τ 8.84 (t, J = 7 Hz, ethoxy group) in a ratio of 1:2:17 as required (areas of all signals between τ 8 and τ 9 were combined.

1(5)-Bicyclo[3.3.0]octene, 58: (112-114)

60 (12 g, 0.06 moles) was placed in a 2.5 ml flask equipped with a short path distillation apparatus and a few crystals of benzoic acid were added. The distilling flask was heated to 180°C for five hours. The distillate was washed with water (2 x 10 ml) and dried (Na_2SO_4 + $CaCl_2$). The clear liquid was purified by chromatography on silica gel using pentane as the eluant. The product was a colourless liquid, yield 5.6 g (86%), b.p. 141 - 142°C (707 torr), n_D^{20} 1.4836; reported (101) b.p. 140 - 141°C (760 torr), n_D^{20} 1.4832.

The i.r. spectrum (neat) showed absorptions at 2900 cm^{-1} (C-H stretch).

The n.m.r. spectrum (CCl_4) showed absorption at τ 7.82 (s).

1(2)- and 1(6)-Bicyclo[4.4.0]decene, 62 and 67: (38,115-118).

Tetralin (100 g, 0.75 moles) was dissolved in ethylamine (500 ml) and dimethylamine (400 g) in a two liter, 3-necked flask equipped with a magnetic stirrer and a dry-ice condenser. The mixture was stirred until it became homogenous and lithium metal ribbon (23 g, 3.3 moles) cut in small pieces was added. The reaction mixture was stirred 12 h and then the dry-ice condenser was removed and the solvent was allowed to evaporate into a dry-ice trap for reuse since the solvent is very expensive. The reaction vessel was fitted with a reflux condenser and water (230 ml) was added over 2 h. The reaction mixture was then filtered and the salts were washed well with ether. The filtrate was extracted with ether (5 x 100 ml) and the combined ether solutions were dried and concentrated to an oil. This oil was distilled to give a clear colourless mixture of 62 and 67, yield 91 g (89%), b.p. 76 - 78°C (15 torr). This mixture was used in the next step without further purification.

1,6-Cyclodecanedione, 64: (38, 116-118).

A mixture of 98% formic acid (125 ml) and 30% hydrogen peroxide (48 ml) was placed in a 500 ml, 3-necked flask equipped with a magnetic stirrer, a reflux condenser, a pressure-equalized dropping funnel and a thermometer,

and stirred for 15 m. The octalin mixture prepared above (42.6 g, 0.3 moles) was added over 1 h, while keeping the reaction temperature at 45 ± 3°C using an ice bath. After the initial reaction had subsided the reaction mixture was kept at 45°C for 5 h by heating and then allowed to stand overnight. The reaction mixture was diluted with water (300 ml) and saturated with sodium chloride and the product was allowed to crystallize overnight at 5°C. The hydroxy formate was filtered off and hydrolyzed in an ice-cold solution of sodium hydroxide (24 g) in water (80 ml). This reaction mixture was stirred at 0°C for 30 m and then at 75°C for 20 m. The mixture was cooled, water (225 ml) was added and the reaction mixture was then stored at 5°C for one hour. The resulting crude trans-diol was collected and dried, yield 42 g (80%).

The crude diol prepared above (36 g, 0.021 moles) was dissolved in benzene (800 ml) and this solution was dried for two hours over anhydrous copper (II) sulphate. Lead tetraacetate (100 g) was added and the reaction mixture was stirred two hours. The mixture was refluxed for one-half hour and then ethylene glycol was added until a test with starch-iodide paper indicated no more oxidant was present. The resulting salts were removed by filtration and the benzene filtrate was washed with water (2 x 100 ml) and dried. Removal of the solvent gave a white solid

which was recrystallized from hexane to give white crystals, 34.6 g (66%), m.p. 101.5-102.5°C, reported (116) 99 - 100°C.

The i.r. spectrum ($CHCl_3$) showed absorption at 1715 cm^{-1} (C=O stretch).

The n.m.r. spectrum ($CDCl_3$) showed two broad overlapping absorptions at τ 7.68 and τ 8.12.

1(7)-Bicyclo[5.3.0]decan-2-one, 65: (38, 116,117).

64 (5.6 g, 0.033 moles) was suspended in saturated aqueous sodium bicarbonate (200 ml) and the mixture refluxed one and one-half hours. After cooling the mixture was extracted with dichloromethane (3 x 75 ml) and the organic extracts were dried. Removal of the solvent gave a light yellow liquid which was distilled to give a clear, colourless oil, yield 4.0 g (80%), b.p. 135 - 137°C (15 torr), n_D^{20} 1.5320; reported (116) b.p. 117 - 119°C (9 torr), n_D^{25} 1.5240.

The i.r. spectrum (neat) showed absorption at 1645 cm^{-1} (C=O stretch).

The n.m.r. spectrum ($CDCl_3$) showed two broad absorptions at τ 7.48 and τ 8.18.

1(7)-Bicyclo[5.3.0]decan-2-ol, 68: (117).

65 (8.5 g, 0.057 moles) was dissolved in distilled methanol (75 ml) and the solution was cooled to -10°C in

an ice-salt bath. Sodium borohydride (7.6, 0.185 moles) was added with stirring, while maintaining the reaction temperature between 0°C and 5°C. The reaction mixture was stirred five minutes and water (100 ml) was added. This solution was extracted with dichloromethane (3 x 50 ml). The organic extracts were dried and concentrated to yield a white solid, pure by tlc, yield 8.4 g (97%), m.p. 53 - 55°C; reported (117) 51 - 52°C.

The i.r. spectrum ($CHCl_3$) showed absorptions at 3375 cm^{-1} (O-H stretch).

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 5.70 (s, OH) and τ 7.3 - 8.7 (broad) in a ratio of 1:16, required 1:15.

1(7)-Bicyclo[5.3.0]decene, 66: (119-121,148,149)

Aluminum chloride (30.6 g, 0.29 moles) was added to ether (12 ml) and stirred until cool. Lithium aluminum hydride (4.4 g, 0.116 moles) was added and the slurry was stirred 15 m. 26 (10 g, 0.067 moles) was dissolved in ether (100 ml) and this solution was added very slowly to the slurry of reducing agents while maintaining the temperature of the reaction vessel at 10°C with a water bath. If this addition is not carried out slowly enough the reaction mixture will decompose vigourously. After the addition was complete the reaction mixture was re-

fluxed for 55 minutes. The resulting suspension was cooled in ice and diluted with ether (200 ml). Sodium sulphate decahydrate was added in small portions with vigourous stirring and cooling in an ice bath until no more hydrogen was evolved and the mixture was pure white. The precipitate was removed by filtration and washed well with ether. The washings and filtrate were combined and washed with water (2 x 75 ml) and dried. Removal of the solvent gave a yellow oil. Distillation in a Kugelrohr apparatus gave a colourless oil which was further purified by chromatography on alumina (Brockman Activity I) using pentane as eluant. The product was obtained as a colourless liquid, yield 5.2 g (57%), b.p. 193°C (700 torr), $\underline{n}_D^{20}$ 1.4937; reported (148) b.p. 95°C (27 torr), $\underline{n}_D^{20}$ 1.4935.

The i.r. spectrum (neat) showed absorption at 2900 cm^{-1} (C-H stretch).

The proton n.m.r. spectrum ($CDCl_3$) showed a broad featureless absorption between 7.5 and 8.8 τ.

The ^{13}C n.m.r. spectrum ($CDCl_3$) showed six signals at (in ppm downfield from TMS) 137.16, 40.03, 30.75, 30.16, 27.76 and 22.39.

Analysis: Calculated for $C_{10}H_{16}$; C, 88.16; H, 11.84; Found: C, 88.41; H, 11.71.

Triethylamine-Borane, 83: (125,150,151)

This was prepared using the method of Bonham and

Drago (152).

Anhydrous triethylammonium chloride (90 g, 0.65 moles) (153) was added in two portions to a stirred slurry of sodium borohydride (30 g, 0.8 mole) in anhydrous tetrahydrofuran (500 ml) contained in a one liter, 3-necked flask. The reaction was carried out in an inert atmosphere of anhydrous, oxygen-free nitrogen. The reaction mixture was stirred two hours and then refluxed for 14 h. Filtration of the reaction mixture through "Celite" and concentration, gave a colourless oil which was distilled to yield a colourless liquid, yield 55 g (92%), b.p. 58 - 61°C (1.5 torr), $\underline{n}_D^{20}$ 1.4420, m.p. -5°C to -3°C; reported (125) $\underline{n}_D^{21}$ 1.4427, m.p. -3°C.

1,5-Cyclododecanediol, 71: (123,127).

This procedure was basically a combination of the procedures of Rotermund and Koster (127) and Fujita and Nozaki (123), and must be carried out using inert atmosphere technique with dry, oxygen-free nitrogen since the intermediate is very oxygen and moisture sensitive.

A mixture of cyclodeca-1t,5t,9c-triene (31 g, 0.2 moles) and triethylamine borane (22.0 g, 0.2 moles) in pure cumene (140 ml) was added dropwise with stirring to cumene (140 ml) at 145°C contained in a one liter, 3-necked flask equipped with an addition funnel, a reflux condenser, a magnetic stirrer and a nitrogen inlet and outlet. The

reaction mixture was cooled and the cumene was removed by vacuum distillation using a nitrogen bleed at 16 torr. The residue from this distillation was transferred to a smaller flask using inert atmospheric technique and was distilled to yield a colourless oil, b.p. 129 - 131°C (17 torr), reported (123), b.p. 122 - 128°C (16 torr). The yield was about 50% of 9b-boraperhydrophenalene.

The borane prepared above was dissolved in cyclohexane (250 ml) and transferred under nitrogen to a 1 liter flask equipped with a magnetic stirrer, a gas inlet and outlet, a reflux condenser and a pressure-equalized addition funnel. Glacial acetic acid (5.76 g, 0.1 mole) in cyclohexane (100 ml) was added and the reaction mixture was refluxed for 30 m under inert atmosphere. The resulting clear solution was cooled to 5°C and a solution of potassium hydroxide (22.5 g) in methanol (375 ml) was added over 10 m. When the reaction mixture had cooled to 5°C a solution of 30% H_2O_2 (32 ml) in methanol (95 ml) was added dropwise over one hour while maintaining the reaction temperature below 10°C. This two-layer mixture was stirred 2 h and then the solvent was removed to give a cloudy oil. 2N potassium hydroxide (375 ml) was added and this solution was continuously extracted with ether for 40 h. Most of the product crystallized in the extractor flask and this was collected to yield 12.3 g of product. The ether extracts were dried and evaporated to an oil which

crystallized to give 2.5 g of product. Total yield of white crystals was 14.8 g (39%), m.p. 154 - 156°C.

The i.r. spectrum ($CHCl_3$) showed absorption at 3250 cm^{-1} (OH stretch).

The n.m.r. spectrum (DMSO-d_6) showed absorption at τ 5.78 (d, OH) and τ 9.70 (broad) in a ratio of 1:11 as required.

The mass spectrum showed no molecular ion but the first fragment was at m$^{\oplus}$-18.

Analysis: Calculated for $C_{12}H_{24}O_2$; C, 71.95; H, 12.08. Found: C, 72.23; H, 12.19.

1,5-Cyclododecanedione, 72: (123,146)

71 (10 g, 0.05 moles) suspended in purified acetone (500 ml) was oxidized with Jones reagent (146) as in the preparation of 51. The crude product was recrystallized from methanol/water to give colourless crystals, yield 7.4 g (75%), m.p. 66.5 - 68.5°C, reported (123) m.p. 66.5 - 67.5°C.

The i.r. spectrum ($CHCl_3$) showed absorption at 1700 cm^{-1} (C=O stretch).

The n.m.r. spectrum ($CDCl_3$) showed a broad, featureless absorption at τ 7.0 - 9.0.

1(8)-Bicyclo[6.4.0]dodecen-9-one, 73: (123)

72 (5 g, 0.025 moles) was dissolved in a solution of

4% potassium hydroxide in methanol (250 ml) and the solution was refluxed for 30 m. After cooling to 5°C and dilution with water (80 ml) the solution was extracted with dichloromethane (4 x 75 ml) and the combined organic extracts were washed with water (50 ml) and dried. Removal of the solvent gave a brown oil which was distilled to yield a faintly yellow liquid, yield 3.9 g (86%), b.p. 99 - 107°C (1.5 torr); reported (123), b.p. 100° (2.5 torr).

The i.r. spectrum (neat) showed absorptions at 1660 cm^{-1} (C=O stretch) and 1625 (C=C stretch), reported (85), 1661 and 1629 cm^{-1}, respectively.

The n.m.r. spectrum showed broad, featureless absorption at τ 7.3 - 8.8.

1(8)-Bicyclo[6.4.0]dodecen-9-ol, 37: (123).

34 (3.6 g, 0.02 moles) dissolved in ether (15 ml) was added dropwise with stirring over 10 m to a suspension of lithium aluminum hydride (2.4 g, 0.06 moles) in ether (40 ml) at -78°C. The reaction mixture was allowed to warm to room temperature and was stirred 5 h. Water (2.3 ml), 2 N sodium hydroxide solution (2.3 ml) and water (7 ml) were added successively and the resulting solid was filtered off and washed with ether. The combined ether solutions were washed once with water (20 ml) and dried. Removal of the solvent gave a colourless oil

which crystallized. Recrystallization from methanol/H_2O gave colourless crystals, yield 3.3 g (91.5%), m.p. 72 - 73.5°C.

The i.r. spectrum ($CHCl_3$) showed absorptions at 3600 (OH stretch, non-hydrogen bonded) and 3440 (O-H stretch, hydrogen bonded).

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 5.96 (methine protons) and τ 7.4 - 8.8 (broad, ring protons) in a ratio of 1:18 as required.

Analysis: Calculated for $C_{12}H_{20}O$; C, 79.94; H, 11.18. Found: C, 79.86; H, 11.18.

1(8)-Bicyclo[6.4.0]dodecene, 74: (128,129).

This reaction was carried out as in the preparation of 66 using 73 (6.0 g, 0.34 moles) in ether (30 ml) added to a slurry of aluminum chloride (15.7 g) and lithium aluminum hydride (2.2 g) in ether (5 ml). Following distillation and chromatography as described, the product was obtained as a colourless oil, yield 3.5 g (63%), b.p. 239° (705 torr), n_D^{20} 1.5020; reported (130) b.p. 62 - 68°C (1 torr), n_D^{25} 1.4995.

The i.r. spectrum (neat) showed absorption at 2900 cm^{-1} (C-H stretch).

The n.m.r. spectrum (CCl_4) showed absorptions at τ 7.6 - 8.2 and τ 8.2 - 8.7, reported (129) τ 7.5 - 8.2 and τ 8.3 - 8.5.

The ^{13}C n.m.r. spectrum ($CDCl_3$) showed six signals at (in ppm downfield from TMS) 130.71, 32.13, 29.75, 29.12, 26.84, and 23.69.

Analysis: Calculated for $C_{12}H_{20}$; C, 87.73; H, 12.27. Found: C, 87.97; H, 12.49.

9,10-Dioxa[3.3.2]propellane, 48:

Ether (4 ml) was placed in a 25 ml three-necked flask equipped with a magnetic stirrer, a powder funnel, a low temperature thermometer and a cold bath at -45°C. When the ether had cooled to -40°C, 98% hydrogen peroxide (1.7 g) was added in three portions allowing the internal temperature to return to -40°C before each addition. When the temperature had returned to -40°C after the last addition, 19 (1.0 g, 9.2×10^{-3} moles) was added. Then 1,3-diiodo-5,5-dimethylhydantoin (1.75 g, 4.6×10^{-3} moles) was added in small portions over 1.5 h never allowing the temperature to rise above -40°C. When all the hydantoin had been added, the reaction mixture was stirred for 15 m at -40°C and then allowed to warm slowly to -25°C. The reaction mixture was poured into ice-water (30 ml) and ether (20 ml) and the organic layer was washed quickly with water (2 x 20 ml), ice-cold 5% aqueous sodium thiosulphate solution until the colour of iodine was just discharged and then once more with water (20 ml). The organic layer was dried at -20° and then concentrated

to one-quarter volume (using an ice bath) and cold (0°C) dichloromethane (30 ml) was added. This solution was again concentrated to one-quarter volume. The dichloromethane solution of the iodohydroperoxide was added to a stirred slurry of silver acetate (5.5 g) in dichloromethane (40 ml) and stirred 15 m at 0°C. The reaction mixture was filtered through "Celite" and the filtrate was washed with water (20 ml), 1% aqueous sodium bicarbonate solution (20 ml), and water (20 ml) and dried. Removal of the solvent at 0°C gave a light yellow oil containing the dioxetane.

This yellow oil was distilled at room temperature (21°C) and 10^{-2} torr, trapping the volatiles at -78°C. The volatile material was a bright yellow oil.

Five such preparations were combined and the bright yellow oily material was chromatographed at -40°C on Silica gel (20 g) using pentane:ether::95:5 as the eluant. Collection of the yellow band from the column followed by evaporation of the solvent at 0°C gave a bright yellow oil which was recrystallized (3x) from isopentane at -78°C to give the product, yield 0.27 g (4%), 92% pure by iodometric titration.

The n.m.r. spectrum (CCl_4) showed absorptions at τ 6.96 (multiplet), τ 7.5 - 8.2 (broad) and τ 8.3 - 8.9 (broad). The signals were all overlapping and no good relative areas could be reported.

Thermolysis of 48:

A sample of 48 in pentane was evaporated to dryness and the flask was stoppered. About 30 s later it was observed that the material in the flask was a white solid and not a yellow liquid. This material weighed 50.0 mg and tlc indicated that two materials were present. Column chromatography on silica gel using ether as the eluant let to isolation of 42.0 mg of white crystals which were identified as 51 by mixed melting point with the authentic material and by tlc. The second component could not be isolated and apparently only a trace was present. The second component was present in the original dioxetane. The yield of product was 42.0 mg (84%).

Reduction of 48:

A solution of 48 (46 mg) in pentane (4.5 ml) was added to a stirred slurry of lithium aluminum hydride (90 mg) in ether (20 ml) at -78°C. The product was isolated as in the preparation of 35. After two coevaporations with benzene (10 ml) to remove any water a white solid (41 mg) was obtained. Thin layer chromatography indicated a faint trace of impurity. The identiy of the product was confirmed to be 57 by mixed melting point (64 - 65.5°C). The yield was 41 mg (86.6%).

11,12-Dioxa[5.3.2]propellane, 49:

This dioxetane was prepared using the method of preparation described for the synthesis of 48 using 66 (2.0 g, 0.015 moles), ether (12 ml), 98% H_2O_2 (2.5 g) and 1,3-diiodo-5,5-dimethylhydantoin (2.75 g, 7.2×10^{-3} moles).

This resulted in a yield of about 2 g of yellow oil. This oil was purified in four portions by column chromatography at -40°C on silica gel using pentane:ether:4:1 as the eluant and collecting the yellow band. The combined products from the four chromatographies were combined and rechromatographed at -40°C as before. The light yellow solid obtained was recrystallized (4x) from isopentane at -78°C. This gave yellow needles, yield 0.65 g (26%), m.p. 57 - 59°C, 99.5% pure by iodometric titration.

The n.m.r. spectrum (CCl_4) showed a broad absorption between τ 7.1 and τ 8.9.

1,7-Bicyclo[5.3.0]decanediol, 79: (38).

66 (0.53 g, 3.9×10^{-3} moles) in ether (15 ml) was added to a solution of osmium tetroxide (1.0 g, 3.9×10^{-3} moles) in ether (40 ml). The reaction was stirred under dry argon for three hours and then allowed to stand 20 h. The ether was evaporated on a hot water bath and a solution of sodium bisulphite (7 g) in water (100 ml) and ethanol (25 ml) was added to the solid residue. This solution was refluxed for 30 h and then filtered. The

ethanol was removed on the rotary evaporator and the remaining solution was extracted with dichloromethane (4 x 30 ml). The organic layers were combined, dried and concentrated to a yellow oil. The diol was separated from the minor amounts of impurities by column chromatography on silica gel using ether as the eluant. The product was a colourless oil, yield 0.45 g (68%). Some of this oil was distilled (2x) in a molecular still to obtain an analytical sample.

The i.r. spectrum (neat) showed absorptions at 3460 cm^{-1} (O-H stretch).

The n.m.r. spectrum ($CDCl_3$) showed absorptions at τ 6.73 (s, OH) and τ 8.38 (broad) in a ratio of 1:10, required 1:8.

The ^{13}C n.m.r. spectrum ($CDCl_3$) showed absorptions at (in ppm downfield from TMS) 82.21, 43.43, 39.27, 30.53, 22.82, and 21.01.

The mass spectrum gave a molecular ion at 170 as required.

Analysis: Calculated for $C_{10}H_{18}O_2$; C, 70.55; H, 10.66. Found: C, 70.56; H, 10.62.

Reduction of 49:

Reduction of 49 was carried out as described for 48, using 49 (50.0 mg, 3×10^{-4} moles). The product was a

colourless oil that was identical in behaviour on thin layer chromatography (in both ether and ethyl acetate) to 79. The product of this reduction was confirmed to be 79 since the two i.r. spectra were identical. Yield of 79 was 46.0 mg (91%).

1(6)-Bicyclo[4.4.0]decen-2-one, 81: (130,131,133).

A: From 66.

66 (0.25 g, 1.83 x 10^{-3} moles) was ozonized with ozone in argon (133) in ethylacetate (40 ml) at -78°C. When a light blue colour was visible in the solution indicated ozonation was complete the solution was allowed to warm slowly to 0°C while passing argon through the solution to remove excess ozone. Then Adam's catalyst (200 mg) was added and the solution was hydrogenated at 0°C and atmospheric pressure. Removal of the catalyst and solvent gave a colourless oil, yield 0.29 g (94%). This material showed absorptions at 3480 and 1705 in the i.r. spectrum and was probably 80.

The product was dissolved in 1% potassium hydroxide in methanol (25 ml) and warmed on a steam bath until thin layer chromatography indicated that the reaction was complete (almost immediately). The reaction mixture was diluted with water (25 ml) and extracted with dichloromethane (3 x 25 ml). The combined organic extracts were washed once with water (50 ml) and dried. Removal of the

solvent gave a light yellow oil, yield 240 mg (92%), n_D^{20} 1.5000, reported (133) n_D^{20} 1.4931. The semicarbazone and the oxime were prepared (42) in 88% and 91% yield, respectively, and had melting points of 243 - 245°C and 147-148°C, respectively; reported (133) 246 - 247°C and 148 - 149°C.

The i.r. spectrum (neat) showed absorption at 1670 cm^{-1} (C=O stretch).

B. From 79

79 (0.045 g, 2.64×10^{-4} moles) was dissolved in dichloromethane (10 ml) and stirred for 2 h with Attenburrow's active manganese dioxide (0.5 g) (152). Removal of the catalyst and solvent gave a partly crystalline oil. This oil was dissolved in ethanol (0.5 ml) and 2 N sodium hydroxide solution (4 drops) was added. After five minutes, a solution of hydroxylamine hydrochloride (0.25 g) in water (1 ml) and 2 N sodium hydroxide (0.5 ml) was added. The oxime was isolated as in A as a white, crystalline solid, yield 30 mg (69%), m.p. 145 - 147°C, reported (133) 148 - 149°C.

Thermolysis of 49:

49 (100 mg, 6.0×10^{-4} moles) was dissolved in benzene (5 ml) and the solution was heated in a sealed tube at 100°C for 15 h. Removal of the solvent gave a partially

crystalline oil. The oxime was prepared from this oil as in B above and isolated as a yellowish crystalline solid, yield 80 mg (89.5%) m.p. 143 - 145°C, reported (133) 148 - 149°C. A mixed melting point with the oxime of 81 prepared above showed no despression of the melting point.

Rates of Chemiluminescence Decay:

Rates of decomposition of the dioxetanes were obtained by measurement of the rate of chemiluminescence decay using a Turner Model 430 spectrofluorimeter with the xenon source lamp turned off. The 60 nm emission monochromator bandwidth was used for maximum sensitivity with the emission monochromator set at 450 nm. The sample cell was a jacketted Pyrex cell with a 10 cm path length and one end of the cell was silvered. The sample was introduced into the middle of the cell which had a capacity of 10 ml. Temperature control was provided by a Colora circulating water bath.

For 48 samples were prepared by measuring out a known volume of a stock solution of the dioxetane and making this up to 10.0 ml with 10^{-2} M DBA or DPA solution. The solvent used here was purified benzene.

For 49 samples were prepared by dissolving weighed samples of dioxetane in 10^{-2} M DBA in purified toluene.

Readings were taken at suitable intervals and the cell temperature was measured before and after each run by placing a thermometer directly into the sample solution.

Activation Energies by the Temperature Change Method:

Samples were prepared as above. The two temperatures were provided by two Colora circulating water baths connected to the spectrofluorimeter in parallel. Temperature equilibration was obtained in two minutes in changing from one temperature to the other. Only DPA was used as the fluorescer in these experiments. Both the temperature-rise and the temperature-drop experiments were done.

Readings were taken at one temperature and then the temperature was changed rapidly and as soon as equilibration had been reached, a second reading was taken. Careful choice of the temperatures used must be made so that virtually no dioxetane decomposes during the equilibration period.

Dependence of Chemiluminescence on Fluorescer Concentration:

Measurements were done using the same experimental apparatus and conditions as described in the kinetics section.

Samples were prepared by mixing 1.0 ml of dioxetane stock solution with known volumes of fluorescer stock solu-

tions and solvent. Benzene was used as a solvent in all cases.

For example, for a solution 10^{-3} M in DBA the sample was prepared by pipetting the following solutions into a clean test tube, 1.00 ml dioxetane stock solution, 1.00 ml 10^{-2} M DBA stock solution and 8.00 ml pure benzene. The sample was well mixed and then placed in the sample cell at the desired temperature. The temperatures used were selected so that the concentration of dioxetane remains constant for the duration of the temperature equilibration period and the measurement period. Samples containing various concentrations of DBA and DPA were used.

For 48 temperature equilibration was complete after 3 m and readings were taken after this time. The reading remained constant for at least 10 m.

For 49 at 69°C considerable outgassing prevented readings from being taken until about 12 m had elapsed. However the reading appeared to be constant over a 15 m period, at least.

BIBLIOGRAPHY

1. J. H. van de Sande, Ph.D. Thesis, University of Alberta, 1968.
2. W. A. Scott, M.Sc. Thesis, University of Alberta, 1973.
3. K. R. Kopecky and J. H. van de Sande, Can. J. Chem., 50, 4035 (1972).
4. K. R. Kopecky, J. H. van de Sande, and C. Mumford, Can. J. Chem., 46, 25 (1968).
5. K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood and Jan-Yih Ding, Can. J. Chem., 53, 1103 (1975).
6. J. E. Baldwin and O. W. Lever, J. Chem. Soc. Chem. Commun., 1973, 343.
7. D. B. Sharp, Absts., 138th Natl. Meeting of Amer. Chem. Soc., New York, N.Y., Sept. 1960, p.79P.
8. K. R. Kopecky and H. J. Reich, Can. J. Chem., 43, 2265 (1965).
9. W. Fenical, D. R. Kearns, and P. Radlick, J. Amer. Chem. Soc., 91, 7771 (1969).
10. C. S. Foote, T. T. Fujimoto and Y. C. Chang, Tetrahedron Lett., 45 (1972).
11. K. Gollnick, D. Haisch and G. Schrade, J. Amer. Chem. Soc., 94, 1747 (1972).

12. N. Hasty, P. B. Merkel, P. Radlick and D. R. Kearns, Tetrahedron Lett., 49 (1972).

13. R. D. Ashford and E. A. Ogryzlo, J. Amer. Chem. Soc., 97, 3604 (1975).

14. M. Maurny and J. Rigaudy, Bull. Soc. chim. Fr., 1487 (1974).

15. J. Scheve and E. Scheve, Zeit. Chem., 14, 172 (1974).

16. C. S. Foote and R. W. Denny, J. Amer. Chem. Soc., 93, 5168 (1971).

17. A. Nickon and J. F. Bagli, J. Amer. Chem. Soc., 83, 1498 (1961).

18. A. Nickon, J. B. DiGiorgio and P. J. L. Daniels, J. Org. Chem., 38, 533 (1973).

19. A. P. Schaap and G. R. Faler, J. Amer. Chem. Soc., 95, 3381 (1973).

20. C. W. Jefford and A. F. Boschung, Tetrahedron Lett., 4471 (1976).

21. C. W. Jefford and A. F. Boschung, Helv. Chim. Acta, 57, 2257 (1974).

22. P. D. Bartlett and M. S. Ho, J. Amer. Chem. Soc., 96, 627 (1974).

23. L. M. Stephenson, D. E. McClure and P. K. Sysak, J. Amer. Chem. Soc., 95, 7888 (1973).

24. M. J. S. Dewar and W. Thiel, J. Amer. Chem. Soc., 97, 3978 (1975).

25. M. J. S. Dewar, A. C. Griffin, W. Thiel and I. J. Turchi, J. Amer. Chem. Soc., 97, 4439 (1975).

26. S. Inagaki and K. Fukui, J. Amer. Chem. Soc., 97, 7480 (1975).

27. N. M. Hasty and D. R. Kearns, J. Amer. Chem. Soc., 95, 3380 (1973).

28. W. Ando, K. Watanabe, J. Suzuki and T. Migata, J. Amer. Chem. Soc., 96, 6766 (1974).

29. P. de Keukeleire, E. Siaens and M. Verzele, Bull. Soc. Chim. Belg., 85, 293 (1976).

30. J. E. Baldwin, G. Höfle and S. C. Choi, J. Amer. Chem. Soc., 93, 2810 (1971).

31. J. E. Baldwin, A. K. Bhatnagar, S. C. Choi and T. J. Shortridge, J. Amer. Chem. Soc., 93, 4082 (1971).

32. K. Kondo, M. Matsumoto and A. Negishi, Tetrahedron Lett., 2131 (1972).

33. Q. E. Thompson, J. Amer. Chem. Soc., 83, 846 (1961).

34. R. W. Murray and M. L. Kaplan, J. Amer. Chem. Soc., 90, 537 (1968).

35. E. Wasserman, R. W. Murray, M. L. Kaplan and W. A. Yager, J. Amer. Chem. Soc., 90, 4160 (1968).

36. P. D. Bartlett and G. D. Mendenhall, J. Amer. Chem. Soc., 92, 210 (1970).

37. R. H. Siegmann, M. J. Beers and H. O. Huisman, Rec. Trav. Chim., 83, 67 (1964).

38. J. E. Filby, Ph.D. Thesis, University of Alberta, 1973.

39. K. R. Kopecky, unpublished results.

40. K. Gollnick, Adv. Ser. Chem., 77, 78 (1968).

41. K. R. Kopecky, P. A. Lockwood, J. E. Filby and R. W. Reid, Can. J. Chem., 51, 468 (1973).

42. R. L. Shriner, R. C. Furon and D. Y. Curtin, "The Systematic Identification of Organic Compounds", John Wiley and Sons, Inc., New York, N.Y., 1964.

43. R. D. Mair and A. J. Graupner, Anal. Chem., 36, 194 (1964).

44. K. B. Wiberg and B. J. Nist, J. Amer. Chem. Soc., 83, 1226 (1961).

45. P. D. Bartlett and A. P. Schaap, J. Amer. Chem. Soc., 92, 6055 (1970).

46. Org. Synthesis, 34, 92 (1954).

47. H. O. House, R. A. Latham and C. D. Slater, J. Org. Chem., 31, 2667 (1966).

48. A. J. Birch, J. Chem. Soc., 809 (1945).

49. K. R. Kopecky and C. Mumford, Can. J. Chem., 47, 709 (1969).

50. T. Wilson and A. P. Schaap, J. Amer. Chem. Soc., 93, 4126 (1971).

51. J. H. Wieringa, J. Strating, H. Wynberg and W. Adam, Tetrahedron Lett., 169 (1972).

52. H. Wynberg and H. Numan, J. Amer. Chem. Soc., 99, 603 (1977).

53. D. J. Bogan, R. S. Scheinson and F. W. Williams, J. Amer. Chem. Soc., 98, 1034 (1976).

54. W. Adam and J. C. Liu, J. Amer. Chem. Soc., 94, 1894 (1972).

55. W. Adam and H. C. Steinmetzer, Angew. Chem. Int. Ed. Engl., 11, 540 (1972).

56. W. Adam, G. A. Simpson and F. Yany, J. Phys. Chem., 78, 2557 (1974).

57. T. Wilson, MTP Int. Rev. Sci. Chem. Kinet., Ser. Two, 9, 265 (1976).

58. W. H. Richardson and W. F. Hodge, J. Amer. Chem. Soc., 93, 3996 (1971).

59. W. H. Richardson, M. B. Yelvington and H. E. O'Neal, J. Amer. Chem. Soc., 94, 1619 (1972).

60. P. D. Bartlett and A. P. Schaap, J. Amer. Chem. Soc., 92, 3223 (1970).

61. C. S. Foote and S. Mazur, J. Amer. Chem. Soc., 92, 3225 (1970).

62. P. R. Story, E. A. Whited and J. A. Alford, J. Amer. Chem. Soc., 94, 2143 (1972).

63. P. S. Bailey, T. P. Carter, C. M. Fisher and J. A. Thompson, Can. J. Chem., 51, 1278 (1973).

64. P. D. Bartlett, A. L. Baumstark, M. E. Landis, J. Amer. Chem. Soc., 95, 6486 (1973).

65. B. S. Campbell, D. B. Denny, D. Z. Denny and L. Shih, J. Amer. Chem. Soc., 97, 3851 (1975).

66. H. H. Wasserman and I. Saito, J. Amer. Chem. Soc., 97, 905 (1975).

67. T. Wilson, M. E. Landis, A. L. Baumstark and P. D. Bartlett, J. Amer. Chem. Soc., 95, 4765 (1973).

68. P. D. Bartlett, A. L. Baumstark and M. E. Landis, J. Amer. Chem. Soc., 96, 5557 (1974).

69. F. McCapra, Chem. Commun., 155 (1968).

70. E. H. White, J.D. Miano and M. Umbreit, J. Amer. Chem. Soc., 97, 198 (1975).

71. W. Adam, J. Chem. Ed., 52, 138 (1975).

72. F. McCapra, Accts. Chem. Res., 9, 201 (1976).

73. G. B. Schuster, N. J. Turro, H. C. Steinmetzer, A. P. Schaap, G. Faler, W. Adam, and J. C. Liu, J. Amer. Chem. Soc., 97, 7110 (1975).

74. T. Wilson, D. F. Golan, M. S. Harris, and A. L. Baumstark, J. Amer. Chem. Soc., 98, 1086 (1976).

75. E. H. White, P. D. Wildes, J. Wiecko, D. Doshan and C. C. Wei, J. Amer. Chem. Soc., 95, 7050 (1973).

76. E. H. White, J. Wiecko and C. C. Wei, J. Amer. Chem. Soc., 92, 2197 (1970).

77. N. J. Turro and P. Letchken, J. Amer. Chem. Soc., 94, 2886 (1972).

78. H. F. O'Neal and W. H. Richardson, J. Amer. Chem. Soc., 92, 6553 (1970).

79. H. E. O'Neal and W. J. Richardson, J. Amer. Chem. Soc., 93, 1818 (1971).

80. H. C. Steinmetzer, A. Yekta and N. J. Turro, J. Amer. Chem. Soc., 96, 282 (1974).

81. N. J. Turro, P. Letchken, N. E. Schore, G. Schuster, H. C. Steinmetzer and A. Yetka, Accts. Chem. Res., 7, 97 (1974).

82. E. J. H. Bechara, A. L. Baumstark and T. Wilson, J. Amer. Chem. Soc., 98, 4648 (1976).

83. P. S. Engel and B. M. Monroe, Adv. Photochem., 8, 245 (1971).

84. V. A. Belzakov and R. F. Vassil'ev, Photochem. Photobiol., 11, 179 (1970).

85. E. H. White, J. Wiecko and D. R. Roswell, J. Amer. Chem. Soc., 91, 5104 (1969).

86. T. R. Darling and C. S. Foote, Pure App. Chem., 41, 495 (1975).

87. T. R. Darling and C. S. Foote, J. Amer. Chem. Soc., 96, 1625 (1974).

88. W. H. Richardson, F. C. Montgomery, and M. B. Yelvington, J. Amer. Chem. Soc., 94, 9277 (1972).

89. W. H. Richardson, F. C. Montgomery, M. B. Yelvington and H. E. O'Neal, J. Amer. Chem. Soc., 96, 7525 (1974).

90. H. E. Zimmerman, G. F. Keck and J. L. Pflederer, J. Amer. Chem. Soc., 98, 5574 (1976).

91. W. Adam, N. Duran, G. A. Simpson, J. Amer. Chem. Soc., 97, 5464 (1975).

92. D. R. Kearns, Chem. Revs., 71, 395 (1971).

93. S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, Chem. Revs., 69, 279 (1969).

94. H. K. Eigenmann, D. M. Golden and S. W. Benson, J. Phys. Chem., 77, 1687 (1973).

95. H. E. O'Neal and S. W. Benson, Int. J. Chem. Kinet., 1, 221 (1969).

96. W. H. Richardson and H. E. O'Neal, J. Amer. Chem. Soc., 94, 8665 (1972).

97. M. A. Umbreit and E. H. White, J. Org. Chem., 41, 479 (1976).

98. C. L. Perrin, J. Amer. Chem. Soc., 97, 4419 (1975).

99. E. Lissi, J. Amer. Chem. Soc., 98, 3386 (1976).

100. E. B. Wilson, J. Amer. Chem. Soc., 98, 3387 (1976).

101. W. T. Borden and T. Ravindranathan, J. Org. Chem., 36, 4125 (1971).

102. W. T. Borden, P. W. Concannon and D. I. Phillips, Tetrahedron Lett., 3161 (1973).

103. L. A. Paquette and R. W. Houser, J. Amer. Chem. Soc., 91, 3870 (1969).

104. L. Field, Synthesis, 101 (1972).

105. E. Vogel, Chem. Ber., 85, 25 (1952).

106. A. C. Cope, J. M. Grisar and P. E. Peterson, J. Amer.

Chem. Soc., 82, 4306 (1960).

107. E. F. Knights and H. C. Brown, J. Amer. Chem. Soc., 90, 5280 (1968).

108. T. Alvik, G. Bergen and J. Dale, Acta Chem. Scand., 26, 1805 (1972).

109. G. I. Glover, R. B. Smith and H. Rapoport, J. Amer. Chem. Soc., 87, 2003 (1965).

110. Kindly supplied by J. Weiner-Fedorak.

111. E. Wenkert and J. E. Yoder, J. Org. Chem., 35, 2986 (1970).

112. G. Crank and F. W. Eastwood, Aust. J. Chem., 17, 1385 (1964).

113. G. Crank and F. W. Eastwood, Aust. J. Chem., 17, 1392 (1964).

114. J. S. Josan and F. W. Eastwood, Aust. J. Chem., 21, 2013 (1968).

115. R. A. Benkeser and E. M. Kaiser, J. Org. Chem., 29, 955 (1964).

116. S. Dev, J. Indian Chem. Soc., 31, 1 (1954).

117. A. G. Anderson and J. A. Nelson, J. Amer. Chem. Soc., 73, 232 (1951).

118. A. C. Cope and G. Holzman, J. Amer. Chem. Soc., 72, 3062 (1950).

119. B. R. Brown and A. M. S. White, J. Chem. Soc., 3755 (1957).

120. J. Broome, B. R. Brown, A. Roberts and A. M. S. White,

J. Chem. Soc., 1406 (1960).

121. E. Kovats, A. Fürst and H. Günthard, Helv. Chim. Acta, 37, 534 (1954).

122. H. Arnold, Chem. Ber., 76B, 777 (1943).

123. S. Fujita and H. Nozaki, Bull. Soc. Chem. Japan, 44, 2927 (1971).

124. S. Hirano, T. Niyama and H. Nozaki, Tetrahedron Lett., 1331 (1973).

125. N. N. Greenwood and J. H. Morris, J. Chem. Soc., 2922 (1960).

126. H. C. Brown and E. Negishi, J. Amer. Chem. Soc., 89, 5478 (1967).

127. G. Rotermund and R. Köster, Ann. Chem., 686, 153 (1965).

128. E. T. Niles and H. R. Snyder, J. Org. Chem., 26, 330 (1961).

129. W. F. Erman and H. C. Kretschmer, Tetrahedron Lett., 1717 (1965).

130. P. S. Wharton and G. A. Hiegel, J. Org. Chem., 30, 3254 (1965).

131. T. K. Stille and R. T. Foster, J. Org. Chem., 28, 2703 (1963).

132. G. Ohloff and W. Giersch, Angew. Chem. Int. Ed. Engl., 12, 401 (1973).

133. M. F. Ansell and J. W. Ducker, J. Chem. Soc., 5219 (1960).

134. N. J. Turro, P. Lechtken and A. Yetka, J. Amer. Chem.

Soc., 95, 3027 (1973).

135. N. J. Turro and P. Lechtken, Pure App. Chem., 33, 363 (1973).

136. J. W. Hastings and G. Weber, Photochem. Photobiol., 4, 1049 (1965).

137. J. Lee and H. H. Seliger, Photochem. Photobiol., 4, 1015 (1965).

138. P. Lechtken and H. C. Steinmetzer, Chem. Ber., 108, 3159 (1975).

139. R. Schmidt, H. C. Steinmetzer, H. D. Brauer and H. Kelm, J. Amer. Chem. Soc., 98, 8181 (1976).

140. N. J. Turro, P. Lechtken, G. Schuster, J. Orell and H. C. Steinmetzer, J. Amer. Chem. Soc., 96, 1627 (1974).

141. N. J. Turro and P. Lechtken, Tetrahedron Lett., 565 (1973).

142. T. Wilson, personal communication with K. R. Kopecky.

143. G. Wolf, Helv. Chim. Acta, 55, 1446 (1972).

144. N. L. Allinger, M. T. Tribble and M. A. Miller, Tetrahedron, 28, 1173 (1972).

145. A. C. Cope and L. L. Estes, J. Amer. Chem. Soc., 72, 1128 (1950).

146. A. Bowers, T. G. Halsall, E. R. H. Jones and A. J. Lemin, J. Chem. Soc., 2548 (1953).

147. E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., (1962), p.267.

148. E. C. Ashby, J. Prather, J. Amer. Chem. Soc., 88, 729 (1966).

149. A. M. Treasurywala, Aldrichemia Acta, 9, 22 (1976).

150. J. Bonham and R. S. Drago, Inorg. Syn., 9, 8 (1967).

151. R. Adams and C. S. Marvel, Org. Syn. Coll. Vol., 1, 531.

152. J. Attenburrow, A. F. B. Cameron and J. H. Chapman, J. Chem. Soc., 1094 (1952).